ADAMS, T. . . 15
Allen, A. H. . . 2
Appleyard, F. . . 3
Arloing, S. . . 15
Arnall, F. . . 3
Arup, P. S. . 4, 12
Autenreith, W. . . 4

BARNETT, E. de B.
Barton-Wright, E. . . 15

Beale, J. F. . . 12
Beasley, H. . . 11
Bennett, R. R. . . 10
Bergeim, O. . . 6, 13
Bloxam, A. G. . . 6
Bloxam, C. L. . . 6
Bolton, E. R. . . 3
Braithwaite, J. O. . 11
Burn, J. . . 10
Burns, D. . . 13
Bywaters, H. W. . 7

CALDWELL, W. . . 6
Cameron, A. T. . . 13
Candy, H. . . 6
Carpenter, J. A. . 4
Castelfranchi, G. . 8
Chauveau, A. . . 15
Clayton, W. . . 2, 5
Clowes, F. . . 3
Cocking, T. T. . . 10
Coleman, J. B. . . 3
Collin, E. . . 11
Collis, E. L. . . 14
Cooley, A. . . 11
Corbin, H. E. . . 8
Cowdry, E. V. . . 15
Cox, H. E. . . 3
Crookes, Sir W. . . 4
Crowther, J. A. . 5, 8

DARLING, H. C. R. 14
Darlington, C. D. . 9
Dexter, J. . . 3
Dible, J. H. . . 12
Dreaper, W. P. . . 5
Duff, A. W. . . 8

EDELMANN, R.
Eichhorn, A.

FIERZ-DAVID, H. E. . 6
Findlay, G. M. . 10
Fleming, G. . . 15
Fourneau, E. . . 6
Fowweather, F. S. . 12
Fresenius, R. . . 7
Fyleman, E. . 5, 6

GATENBY, J. B. .
Gibbs, W. E. .
Gilmour, C. R. . 13
Giltner, W. . . 12
Gimlette, J. D. . 14
Giua, M. . . . 7
Glasstone, S. . 8
Graves, B. . . 15
Gray, A. . . . 8
Green, J. R. . 9
Greenish, H. G. 11
Greenwood, M. 14
Groves, C. E. 7

HACKH, I. . . . 2
Hampshire, C. H. . 11
Harrison, G. A. . . 12
Harshberger, J. W. . 9
Haslam, J. F. C. . 14
Hatschek, E. . . 5
Hawk, P. B. . 6, 13
Henry, T. A. . . 7
Hewer, H. R. . . 15
Hewlett, R. T. . 12, 14
Hodges, F. W. . . 3
Hodgkinson, W. R. . 4
Holder, J. T. . . 15
Hood, G. F. . . . 4
Horwood, A. R. . 9
Hunter, H. . . . 9

IMMS, A. D. . . . 15
Ineson, W. I. . . 7

JAMESON, W. W. . 14
Jensen, H. R. . . 2
Jobling, E. . . . 5
Johnson, A. E. . 6, 7
Johnston, J. H. . . 12

KIRK, J. B. . . . 14
Kloes, J. A. van der 6

LATHROP, E. C. . 2
Leake, H. M. . 9
Lee, A. B. . . 15
Lelean, P. S. . 14
Lewis, S. Judd . 6
Liverseege, J. F. 14
Lloyd, D. J. . . 3
Lucas, C. E. L. . 11
Lucas, E. W. . 10
Lyons, C. G. . 3

MACBRIDE, E. W. 15
Macfadyen, A. . 13
Mackie, H. B. . 11
Maplestone, P. A. 15
Marshall, A. . . 7
Marshall, C. E. . 12
Mason, F. A. . 6
Maxted, E. B. . 5
Mayneord, W. V. 8
McIntosh, J. . . 12
Mitchell, C. A. 2, 5, 6, 7

Mohler, J. R. .
Molinari, E. .

NANKIVELL, A. T.
Newman, F. H. .
Nierenstein, M. .
North, W. . .

ORLA-JENSEN . .

PARKINSON, G. S. .
Parry, E. J. . . .
Pauli, W. . . .
Philp, J. . . . .
Piney, A. . . .
Pope, T. H. . . .
Porter, A. E. . .
Pregl, F. . . . .
Pryde, J. . . .

ROBINSON, G. W. .
Robson, J. M. . .

SADTLER, S. S. . .
Sansome, F. W. . .
Searle, A. B. . .
Silvester, W. A. .
Simpson, R. H. . .
Small, J. . . . .
Smith, K. M. . .
Spear, R. H. . .
Stead, G. . . .
Stevens, H. B. . 10,
Stevens, W. C. . .
Stewart, A. M. . .
Stiles, W. S. . . .
Stockdale, D. . .
Suckling, E. . . .
Sutton, F. . . .
Sutton, W. L. . .
Svedberg, T. . .

THORNE, P. C. L. .
Thresh, J. C. . 12,
Tilden, Sir A. W. .
Tognoli, E. . . .

VACHER, A. . . .
Valentin, W. G. . .
Villavecchia, V. . .

WAESER, B. . . .
Wagner, R. . . .
Wallis, T. E. . .
Walsh, J. W. T. .
Warren, W. H. . .
Watts, H. . . .
Whitby, L. E. H. . 1
White, F. D. . . 1
Whymper, R. . .
Wiley, H. W. . . 1
Williams, H. E. . .

YORKE, Warrington 1

7, 34.

RECENT ADVANCES IN ATOMIC PHYSICS

By G. Castelfranchi. Translated and Edited by Dr. W. S. Stiles and Dr. T. W. T. Walsh. Two Volumes.
Ready May, 1932

RECENT ADVANCES IN PHYSICAL CHEMISTRY

By Samuel Glasstone, Ph.D., D.Sc., F.I.C.
32 Illustrations. **15s.**

RECENT ADVANCES IN ANALYTICAL CHEMISTRY

Edited by C. A. Mitchell, D.Sc., F.I.C. Written by Specialists.
Volume I.: Organic. 25 Illustrations. **15s.**
Volume II.: Inorganic. 26 Illustrations. **15s.**

RECENT ADVANCES IN MICROSCOPY (Biological)

Edited by A. Piney, M.D., M.R.C.P. Contributions by Basil Graves, *M.C.*, D.O.M.S.; E. W. MacBride, D.Sc., F.R.S.; H. R. Hewer, A.R.C.S.; and E. C. Barton-Wright, M.Sc. 83 Illustrations. **12s. 6d.**

RECENT ADVANCES IN BIOCHEMISTRY

By John Pryde, B.Sc., M.Sc. Third Edition.
42 Illustrations. **12s. 6d.**

J. & A. CHURCHILL

RECENT ADVANCES IN PHYSICS
(NON-ATOMIC)

By

F. H. NEWMAN
D.Sc. A.R.C.S., F.Inst.P.
Professor of Physics, University College of the
South-West of England, Exeter

With 51 Illustrations

LONDON
J. & A. CHURCHILL
40 GLOUCESTER PLACE
PORTMAN SQUARE
1932

Printed in Great Britain

PREFACE

THIS book is an attempt to give the reader some idea of the chief advances in physics, mainly "non-atomic," that have been made during the past few years. Owing to the rapid changes which are now taking place in several of the subjects discussed, and the fact that approximately 4,000 papers, embodying the results of original work in physics, are published annually, it is impossible to write a complete account of all of these advances in all branches. One is compelled to select certain parts. It is not an easy matter to make such a selection, and the author cannot hope that the particular choice, which seems to him the best, will necessarily appeal to all readers, but, as far as possible, the selection has been made representative of the most important advances. Omissions of important results, some of which another author would very likely have considered essential to include, are unavoidable. In addition, it seemed preferable to describe the parts included in some detail, rather than make the book a mere collection of references.

One cannot divide physics into "atomic" and "non-atomic" branches, nor is it desirable that any attempt to do so should be made. Indeed, the whole trend of present-day science is, as it should be, towards correlation. For this reason some so-called "atomic physics" has been included. Electromagnetic radiations and magnetism are both treated rather extensively because the enormous number of facts associated with these subjects can be correlated in terms of general principles, and the progress of all science is marked by the discovery of relations between facts, apparently unconnected.

Throughout the work numerous references are given in footnotes to scientific literature, and these should be consulted by the reader who wishes to obtain more detailed information concerning any given part of the subject. As the literature has been freely utilised, it is hoped that adequate credit has been accorded at the appropriate places in the text. A bibliography is given at the end of each chapter, and since all such bibliographies must necessarily be incomplete, the main principle in the compilation has been to include a representative selection in each branch of the work.

F. H. N.

EXETER.

CONTENTS

PAGE

Preface . . . v

I. The Wave-like Character of Matter . . . 1

1. Introduction. 2. Wave Mechanics. 3. Electron Waves. 4. Refraction of Electrons. 5. Polarisation of the Waves. 6. The Applications of Electronic Diffraction. 7. The Wave Characteristics of Free Atoms and Molecules. 8. The Existence of Waves. Bibliography.

II. Statistical Mechanics 21

1. Introduction. 2. State, or Phase, Space of a System. 3. The New Statistics. 4. The Distribution Function in a Degenerate Gas. 5. Comparison of the Statistics Theories. 6. Application of Fermi-Dirac Statistics to the Electron Theory of Metals. 7. Zero-point Energy and Specific Heat. 8. The Fermi Distribution for an Electron Gas. 9. The Susceptibility of Metals. 10. Electrical Conduction. 11. Thermal Conduction. 12. Potential Difference. 13. Thermionics. 14. Photo-electricity. 15. Electron Emission in Intense Electrical Fields. 16. Thermo-electric Phenomena. Bibliography.

III. The General Properties of Matter 55

1. High Pressure Effects. 2. The Effect of Pressure on Thermal Conduction. 3. The Effect of Pressure on Electrical Properties. 4. High Vacuum Technique. 5. The Flow of Gas at very Low Pressures through a Hole in a Thin Plate. 6. Surface Tension and Thin Films. 7. Adsorption on Solids. 8. Viscosity of Liquids. Bibliography.

IV. Acoustics 97

1. Velocity of Sound in Liquids. 2. Explosive Sounds of Long Range. 3. High Frequency Vibrations. 4. Piezo-electric Resonators. 5. Piezo-electric Stabi-

CHAP.

lisers and Oscillators. 6. Ultra-sonic Waves. 7. The Intensity of Sound. 8. Architectural Acoustics. 9. Sound Ranging. 10. Electro-acoustics. 11. The Reproduction of Sound. 12. Wave Filters. Bibliography.

V. **Low Temperatures** 143

1. The International Temperature Scale. 2. Very Low Temperatures. 3. The Measurement of very Low Temperatures. 4. Specific Heats at very Low Temperatures. 5. The Thomson Effect at Low Temperatures. Bibliography.

VI. **Electromagnetic Radiations** 158

1. The Range of Electromagnetic Radiations. 2. Electric Waves. 3. Ultra-short Electric Waves. 4. Infrared Spectra. 5. Oscillation Bands. 6. Rotation Bands. 7. Oscillation-rotation Bands. 8. Infra-red Spectra of Gases. 9. Infra-red Spectra of Liquids. 10. Infra-red Spectra of Solids. 11. The Application of Band Spectra to Two Types of Hydrogen. 12. The Raman Effect. 13. The Intensity and Polarisation of Raman Lines. 14. The Raman Effect in Gases and Vapours. 15. The Raman Effect in Liquids. 16. The Raman Effect in Solids. 17. Theory of the Raman Effect. 18. The Extreme Ultra-violet Region of the Spectrum. 19. Ultra-violet Photomicrography. 20. The Measurement of X-ray Wave-lengths. 21. Determination *of the Values of Physical Constants.* 22. The Refraction of X-rays. 23. The Scattering of X-rays. 24. X-ray Diffraction in Liquids. 25. Gamma-rays. 26. Cosmic Rays. 27. The Velocity of Light. Bibliography.

VII. **Magnetism** 236

1. The Magnetic Properties of Atoms. 2. The Magnetic Deflection of Atomic Rays. 3. Diamagnetism. 4. Experimental Results. 5. Diamagnetism of Molecules. 6. Diamagnetic Crystals. 7. Diamagnetism in the Paramagnetic Elements. 8. Paramagnetism. 9. The Magneton. 10. Susceptibility of Ions. 11. Low Temperature Results. 12. Paramagnetic Gases. 13. Ferromagnetism. 14. Atomic Moments of Ferromagnetics. 15. Magnetisation of Single Crystals. 16. Magneto-thermal Phenomena. 17. Magneto-

CHAP.

mechanical Effects. 18. The Barkhausen Effect. 19. The Gyromagnetic Effect. 20. Magneto-resistance Effects. 21. Intense Magnetic Fields. 22. Electrical Conduction in Intense Magnetic Fields. 23. Theories of Ferromagnetism. Bibliography.

VIII. Electricity 325

1. Electric Moment and Dielectric Constant. 2. Atmospheric Electricity. 3. Ozone in the Atmosphere. 4. Thunderclouds. 5. Lightning. 6. The Conduction of Electricity through Solutions. 7. Solvation of the Ions. 8. Dimensions of Ions. 9. Theories of Electrolytic Conduction. 10. The Dielectric Constant of Electrolytic Solutions. 11. The Wien Effect. 12. Conduction Dispersion. 13. Superconductivity. Bibliography.

Name Index . . 366

Subject Index . 372

RECENT ADVANCES IN PHYSICS

CHAPTER I

THE WAVE-LIKE CHARACTER OF MATTER

1. Introduction. During the past few years it has become increasingly evident that the classical theory of radiation is not capable of explaining certain classes of phenomena, especially those concerned with the interaction between radiation and matter. Not that we question in any way the wave character of light, as witness the striking successes of this conception in explaining polarisation and interference of light, but that there are certain other properties of light which cannot be interpreted in terms of waves, *e.g.*, the phenomenon of photo-electric emission. It is imagined that the energy of a beam of light is carried by corpuscles, called *photons*, each having a definite energy, $h\nu$, and momentum, depending on the frequency ν of the light. Disregarding the phenomenon of interference, with which this idea apparently conflicts, the photons must possess momentum $h\nu/c$, h being Planck's constant and c, the velocity of light. We can then explain the observations on light pressure in terms of impinging particles. These photons seem to possess as real an existence as electrons, or any other particle known in physics. Further striking evidence supporting this photon hypothesis was supplied by the discovery of the Compton effect * with X-rays. Yet with these same X-rays interference experiments can be conducted just as well as with ordinary light.

Formerly, it was generally accepted that electrons, unlike light waves, were corpuscular in nature, and moved along definite paths. Under certain circumstances they can be counted as they pass a point, so that their energy and electric charge are distributed discontinuously, at least at certain times. Recent experiments have shown, however, that definite interference effects can be obtained with a beam of electrons.

---

* See Section 23, Chapter VI.

These facts suggest an intimate connection between waves and particles, not only in the case of light, but also in the case of all particles. The photons seem to be controlled by waves in a manner which cannot be understood from the point of view of ordinary mechanics. The same applies to other particles, although the influence of the waves on the motion of such particles becomes less noticeable as their mass increases.

The old classical ideas will not account for this behaviour. Indeed we must look upon the waves and particles as two abstractions which we find useful for describing the same physical reality, although it is incorrect to picture this reality as containing, at one and the same time, both waves and particles. We cannot construct any mechanism which, acting according to the classical laws, correctly describes their connection and accounts for the motion of the particles. This difficulty, together with others which arise when the classical theory of electrodynamics is applied to atomic phenomena, has been solved by departing fundamentally from the laws and concepts of classical mechanics, and introducing a new system of mechanics called *quantum mechanics.* It is based on general laws, and although there are very few changes made in the classical theory, these changes are fundamental in nature, involving the introduction of entirely new concepts. Yet at the same time most of the features of the classical theory reappear unchanged in the new theory.

The various formulations of quantum mechanics, proposed by different investigators, are to a large extent fundamentally equivalent. They include :

(1) Born and Heisenberg's matrix theory.*
(2) Schrödinger's wave mechanics.†
(3) Dirac's theory of q numbers.‡

---

* *Zeits. f. Phys.*, **34**, 858 ; **35**, 557 (1925–1926).

† "Wave Mechanics" (1928).

‡ *Proc. Roy. Soc., A*, **109**, 642 ; **110**, 561 ; **111**, 281 (1925–1926).

(4) Born and Wiener's operator theory.*

(5) The transformation theory.†

Those under headings (1) and (2) are the commonest, but that under (5) is the most comprehensive and far-reaching, as it includes the others as special cases. The theories of Heisenberg, Born, Jordan and Dirac are essentially those of discontinuities, whereas the so-called wave mechanics starts from the basis that all mechanics, including quantum mechanics, is ultimately dependent on a wave motion, the solution of a mechanical problem being the solution of the partial differential equations of an appropriate wave motion. Although this is a theory whose basis is essentially one of continuity, it is remarkable that the results of the two theories are mathematically identical.

2. Wave Mechanics. The origin of wave mechanics is due to de Broglie,‡ who generalised the idea that a corpuscle, like a wave, has a frequency associated with it. He suggested that all forms of energy have an atomic structure similar to that of matter, and that the atoms of energy are grouped round certain singular points, forming electrons, photons and such-like particles. Inspired by these new ideas of de Broglie,‡ Schrödinger § developed a theory in which the solution of problems in quantum mechanics was made to depend upon the solution of a differential equation, the wave equation, in which the energy of the system appeared.

Now from the Hamiltonian dynamics, upon which the foundations of wave mechanics are built, it can be shown || that the motion of a particle in a field of force may be represented as a ray of a propagated wave surface. All classical dynamics is composed of the motion of particles, and can therefore be equally well regarded as wave motions with the energy travelling along certain rays, the paths of the particles. The energy velocity of the light waves in the optical problem is equal to the energy velocity in the dynamical motion of a particle.

---

[*] *Zeits. f. Phys.*, **36**, 174 (1926).

[†] *Proc. Roy. Soc., A.*, **113**, 621 (1927); "Quantum Mechanics," Dirac, (1930); *Zeits. f. Phys.*, **44**, 1 (1927).

[‡] "Ondes et mouvements" (1926).

[§] *Loc. cit.*

[||] *Proc. Phys. Soc.*, **39**, 171 (1926).

The motion of a particle, adequately described according to the classical theory of mechanics by giving its co-ordinates x, y, z, as functions of the time variable, t, is, according to the new theory, to be described by considering a definite wave motion which occurs among waves of definite frequency and velocity. This is a fundamental idea in wave mechanics, but the statement does not necessarily mean that the wave motion really exists.

If we are to formulate a wave theory of mechanics, valid down to atomic dimensions, it must coincide with the Hamiltonian theory on the large scale. Schrödinger made this extension by formulating a partial differential equation to govern the changes of a new and important quantity ψ, ordinarily called the amplitude of the *matter waves*, *i.e.*, the waves associated with moving particles.

The wave equation suggests the association of a wave-length $\lambda = h/mv$ with the particle, where m is its mass and v, its velocity. If we agree to measure the wave-length in Ångstrom units (Å) then for a free electron,

$$\frac{12\cdot 25}{\sqrt{\ }}\ \text{Å units} \qquad (1)$$

where V is the potential difference through which the electron must fall in order to attain the velocity v. Thus, an electron which has been accelerated through 150 volts is associated with a wave-length of nearly 1 Å.

3. Electron Waves. Elsasser * predicted that there would be a diffraction of such electrons when they impinge on a crystal, such as is used in X-ray diffraction experiments, but Davisson and Germer † were the first to detect experimentally this diffraction phenomenon. They directed a narrow beam of electrons against the face of a nickel crystal, and observed that under certain conditions a sharply defined beam of electrons left the crystal in the direction of regular reflection, the angle of reflection being equal to the angle of incidence. The experimental arrangement is shown in Fig. 1. The essential parts of the apparatus are the "electron gun," G, which supplies a steady stream of electrons from a filament, the crystal, or target, T, against which the electrons are projected, and the double Faraday box collector, C. High-speed electrons, scattered within the small solid angle defined by the collector opening, enter the inner box of the collector, and thence pass through a sensitive galvanometer. The angle between the axis of the incident beam and the line joining the bombarded area with the opening in the collector could be varied from 20° to 90°. Also the target could be rotated about an axis that coincides with the axis of the incident beam. It was thus possible to measure the intensity of the scattering in any direction in front of the target, with the exception of directions lying within 20° of the incident beam, and to construct curves showing the current received by the collector as a function of the angle. Such a curve for an angle of incidence of 30°, and a bombarding potential of 83 volts, is shown in Fig. 2. There is a sharp spur protruding from the curve exactly in the direction of regular reflection.

---

* *Naturwiss.*, **13**, 711 (1925).

† *Phys. Rev.*, **30**, 705 (1927).

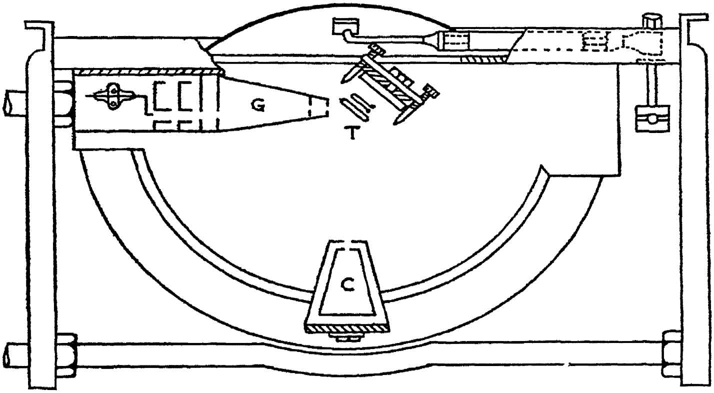


FIG. 1.—Diffraction of electrons. (Davisson and Germer.)

Now it will be remembered that X-ray reflection is characterised by marked selectivity. If a beam of monochromatic X-rays is directed against a crystal face, the intensity of the beam, reflected at a certain angle, is very nearly zero, unless the wave-length of the beam is near, or at, one or other of a series of discrete values. The same effect is exhibited by electrons. When the intensity of the reflected beam is measured as a function of the speed of bombardment, it passes through one maximum after another, as

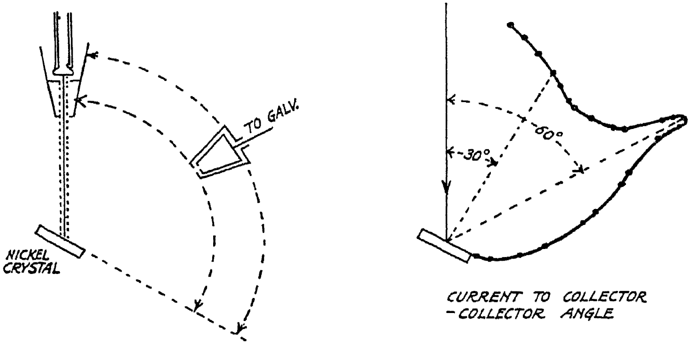


FIG. 2.—Experimental arrangement for investigating the scattering of electrons by a crystal, and a typical curve showing beam of regularly reflected electrons.

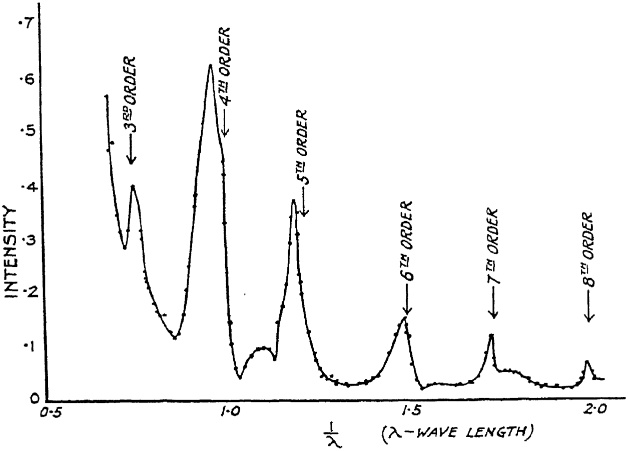


FIG. 3.—Diffraction of electrons. (Different orders.)

the speed is increased. A curve exhibiting this behaviour is shown in Fig. 3.

Thomson * has studied the diffraction of beams of high-speed electrons—15,000 to 60,000 volts—by extremely thin metal foils. He observed that electrons of these speeds are diffracted by polycrystalline metal in the way familiar to us in the powder form of X-ray diffraction. The cross-section of the transmitted beam consists of a central spot, surrounded by a number of concentric rings. The latter correspond to the rings that would be observed if the incident beam were one of X-rays of wave-length equal to h/mv, where m is the mass of the electron when moving with a speed v.

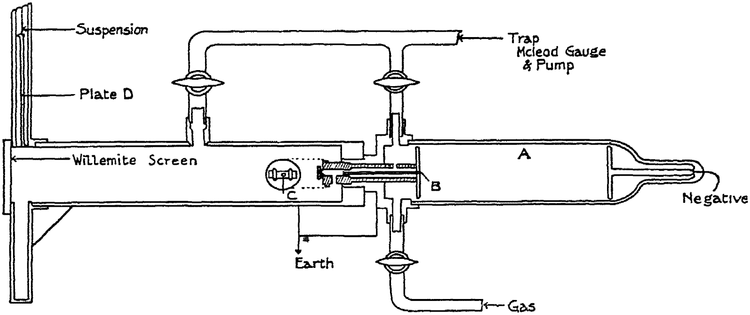


FIG. 4.—Experimental arrangement for investigating the scattering of electrons by thin metal foil. (Thomson.)

The beam of approximately homogeneous cathode rays was sent through the thin film at normal incidence and received on a photographic plate at some distance behind. The film must be so thin that the electron in its passage through it is only scattered once, otherwise the pattern will be hopelessly blurred by the superposition of deflections, and will appear on the photographic plate as a nearly uniform blackening, except perhaps for an increased intensity near the place corresponding to the direction of the original beam. In the experiments cathode rays, generated by an induction coil, in the tube A, Fig. 4, pass through a fine

---

* *Proc. Roy. Soc., A.*, **117**, 600 (1929).

tube, B, and film mounted at C. D is the photographic plate and can be lowered by means of a magnetic release.

With films of Al, Au and celluloid the general effect was that of a series of concentric rings round the spot made by the undeflected beam. In some cases these rings were of uniform intensity round the circumference; in others the intensity was more or less concentrated in a series of spots on the circumference. There was no doubt that the whole pattern was due to cathode rays, because in the absence of the film only a central spot was seen, and a magnet brought up between C and D deflected the whole pattern.

Suppose that the beam of cathode rays is incident at a glancing angle θ, on a plane of indices h, k, l, of a small element of crystal. According to the usual Bragg formula, it will be selectively reflected provided that $2d \sin \theta = \mathrm{n}\lambda$, where d is the distance between the successive atom planes and n is an integer. If L is the distance of the photographic plate, the diffracted beam will give rise to a mark on the plate at a distance $D/2$ from the central spot, where

$$D = 4\theta L = 2\mathrm{n}\lambda L/d,$$

assuming θ to be small.

If allowance is made for the variation of mass of an electron with velocity in the acceleration of the cathode rays, equation (1) becomes:

$$\lambda = \frac{12{\cdot}25}{\sqrt{\mathrm{V}}}\left(\begin{matrix} - \\ 1 \end{matrix} \qquad 1200\ m_0c^2 \right)$$

where **e** is the electronic charge and m_0, its speed, supposed very small compared with the velocity of light. Thus if D is the diameter of any given ring, $D\mathrm{V}^{\frac{1}{2}}\ (1 + \mathbf{V}\mathbf{e}/1{,}200\ m_0c^2)$ should be constant. Thomson found that this was so.

If a large number of small crystals are present, arranged at random, so that some are present at all angles, we shall have a ring of diameter given by the above formula for every spacing d in the crystal lattice and n = 1, 2, 3, *etc.* This is the Hull-Debye Scherrer pattern for powdered crystals. If the crystals have definite orientations with respect to the film, some of these rings will be absent. Thus, consider a crystal el, deposited on a metal angular axes, and suppose a (100) face is always approxima reflecting surface so film surface ; we shall have reflections at (010) and (011) faces, because the small angle θ required can be provided by the slight divergence of the cathode ray beam and by lack of flatness in the film. On the other hand, reflection from (111) face will not appear, because the rays would have to make a large angle with the plane of the film in order to be incident on face (111) at the small angle required by Bragg's law, $n\lambda = 2d \sin \theta$, remembering that λ is of the order of 1/50*th* that of d. If, further, crystals are so oriented that not merely is one axis perpendicular to the film, but the axes in the film are not arranged at random, then the rings which do appear will not be of uniform intensity, each direction of the axes giving rise, in the case of cubic symmetry, to four spots on the circumference of the ring.

With aluminium films the thickness was probably of the order 10^{-5} cm. Besides an inner ring of diameter D_1, two others of diameters D_2 and D_3 could be distinguished outside it. The ratio $D_2/D_1 = 1{\cdot}40$, and $D_3/D_1 = 2{\cdot}08$. These ratios correspond to $\sqrt{2} : 1$ and $2 : 1$. Now aluminium is found from X-ray experiments to have a face-centred cubic lattice. For such a lattice the distances d between the planes are given by $d = a/(h^2 + k^2 + l^2)^{\frac{1}{2}}$ where h, k, l, are the indices of the plane and a, the side of the unit cube. If some of the quantities h, k, l, are odd and some even, counting zero even, all are to be doubled. Now if one axis is perpendicular to the film, the possible planes are those for which one index is zero and smallest value of h, k, l are, respectively, (100), (110), (120), *etc.* But $D = 2n\lambda L\ (h^2 + k^2 + l^2)^{\frac{1}{2}}/a$, hence doubling the indices when required, we have in succession $Da/L\lambda = n4,\ n4\sqrt{2},\ n4\sqrt{5}$, *etc.* If we put $n = 1, 2$, in the first, and $n = 2$ in the second, we obtain $Da/L\lambda = 4,\ 4\sqrt{2}$, or 8, *i.e.*, in the ratio $1 : \sqrt{2} : 2$, as found for $D_1 : D_2 : D_3$. The value of a works out to be $3{\cdot}8 \times 10^{-8}$ cm., and by X-ray analysis its value is $4{\cdot}046 \times 10^{-8}$ cm.

Thomson * has also described the cathode ray diffraction ng for the following metals : silver, lead, iron, nickel, and al with tube, B, and film mo[illegible]sten. Of these, nickel shows an unexpected structure, namely, hexagonal closest packing, the rest give results in full agreement with the structures deduced from X-ray analysis of the metals, except for certain films formed from lead and iron, which probably contained compounds. He measured the slowest speed of rays for which rings were visible, the voltage varying from 10,500 to 15,500, the higher voltages being required for the thicker films. Attempts to get rings with 300-volt electrons were unsuccessful.

---

* *Proc. Roy. Soc., A.*, **125**, 352 (1929).

By photometric measurements of the diffraction rings in gold a curve was deduced giving the variation of wave scattering with angle for the individual atoms. The curve obtained falls much more steeply than the corresponding X-ray curve.

Rupp [*] used a ruled grating to diffract the electrons. A beam was allowed to fall at almost grazing incidence upon a grating of speculum metal with 1,300 rulings per cm. The regularly reflected beam was caught upon a photographic plate, which recorded diffracted beams up to the third order. The electrons came from barium oxide and passing through three slits in series, fell upon a grating from which the beam passed on to the photographic plate. About forty photographic records were made, there being three different angles of incidence with the grating and three distinct velocities of the electrons, determined by the voltage through which they fell. The entire apparatus was in a vacuum. The results obtained agreed with de Broglie's formula.

Other experiments by Rupp [†] show that as the angle of incidence decreases the proportion of electrons reflected at the equal angle of reflection increases (silver) ; that the electrons reflected regularly without energy loss increase in quantity with decrease in electron velocity, the angle of incidence being kept constant ; that for elements in the same vertical column of the periodic table the intensity of the reflection maximum increases with decreasing ordinal number. Definite experimental proof of the total reflection of electrons was provided by an experiment in which the incident beam impinged on a thin wedge of nickel, deposited on a metal (Cu) or insulator (KCl). On displacing the reflecting surface so that the point of incidence moved along the metal wedge, the intensity of the reflected electrons showed, for angles of incidence in the neighbourhood of 80°, a characteristic maximum which was due to total reflection of the electrons at the interface Ni-Cu or Ni-KCl, respectively.

---

[*] *Zeits. f. Phys.*, **52,** 8 (1928). See also *Ann. d. Phys.*, **9,** 458 (1931).

[†] *Phys. Zeits.*, **30,** 935 (1929).

Kikuchi * has obtained some remarkable photographs of the diffraction of high-speed electrons by mica. The molecules in the cleavage face of mica form a triangular array, and in some photographs the patterns are just those which would be formed if the diffracting system were a single layer of molecules. The specimen was, however, fifty or more layers in thickness, and it is interesting to know how a crystal comprising so many layers can produce the pattern of a two-dimensional grating. A possible explanation is to be found in the lack of coherence among the waves proceeding from the different layers. The wave-lengths of the waves used in test experiments were only about 1/200th of the distance between the successive layers of molecules, so that only very slight departures from the normal spacing are sufficient to produce complete incoherence and the observed pattern. Such departures are easily imagined in a crystal which cleaves as readily as mica, and in a thin specimen which has been subjected to considerable manipulation. As the thickness of the crystal is increased, there is a gradual development of the features characteristic of diffraction by three-dimensional gratings.

In connection with these results Bragg and Kirchner † have shown, from certain experiments on electron diffraction by very small crystals, that the third condition for interference, namely, that depending on the repeat of the crystal pattern in the direction of the incident beam, disappears, giving a two-dimensional grating effect. This condition becomes inoperative for a crystal of thickness equal to 100 Å units.

4. Refraction of Electrons. Davisson and Germer found that the diffracted electron beams did not coincide in direction exactly with any of the principal Laue beams, *i.e.*, they did not appear to be regularly reflected from any of the principal planes of the crystal. This was shown to be due to the refracting nature of the crystal for electrons.

---

* Imp. Acad. Tokyo, *Proc.*, **4**, 354, 471 (1928).

† *Nature*, **127**, 738 (1931).

Imagine a beam of radiation incident normally upon the surface of a crystal, of which the refractive index is n. The wave-length outside the crystal being λ that inside it is λ' where $\lambda' = \lambda/n$. There is no change in direction as the beam enters the crystal, and the beam of wave-length λ' meets a certain set of atom planes at an angle θ, Fig. 5. A regularly reflected beam moves off from these planes provided that :

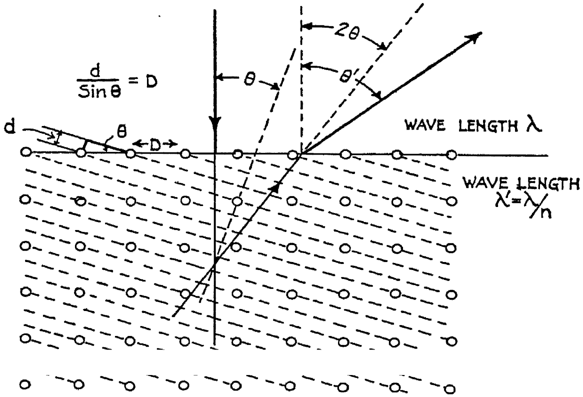


FIG. 5.—Diffraction and refraction of electrons by a crystal.

$$\lambda' = (2d\cos\theta)/n.$$

This beam meets the crystal surface at an angle 2θ, but is refracted on passing through the surface, and leaves the crystal in the direction θ'. The beam issuing from the crystal appears therefore not to be regularly reflected from any of the principal planes.

Treating the electron radiation as if it were light, and writing

$$n = \lambda/\lambda' = \sin\theta'/\sin 2\theta,$$

we have,

$$\lambda' = \lambda\sin 2\theta/\sin\theta'.$$

By Bragg's law,

$$\lambda' = (2d \cos \theta)/\text{n}.$$

Equating these expressions for λ' and solving for λ we obtain :

$$\lambda = (2d \cos \theta \sin \theta')/\text{n} \sin 2\theta.$$

Writing $2 \sin \theta \cos \theta$ for $\sin 2\theta$ and eliminating $2 \cos \theta$, this reduces to

$$\lambda = (d \sin \theta')/\text{n} \sin \theta.$$

Since $d/\sin \theta = \text{D}$, the distance between adjacent atoms in the surface of the crystal, $\lambda = \text{D} \sin \theta'/\text{n}$. This is an extremely useful relation, as it enables the wave-length of the diffracted beam to be calculated (provided its order n is known) from the distance between lines of atoms in the surface of the crystal and the angle at which the beam emerges. In one case for the nickel crystal, the beam was observed, when the bombarding potential was 54 volts, at $\theta' = 50°$. Since $\text{D} = 2{\cdot}15$ Å, the wave-length of the " 54-volt electrons " should be given by :

$$\lambda = 2{\cdot}15 \text{ n} \sin 50° = 1{\cdot}65 \text{ n}.$$

But this was the first beam to appear, so that $\text{n} = 1$ and $\lambda = 1{\cdot}65$ Å. From equation (1), $\lambda = 1{\cdot}67$ Å, which is in good agreement with the experimentally determined value.

Davisson and Germer plotted the intensity of the reflected electron beam for an angle of incidence of 10° against the inverse wave-length of the electron waves, and obtained a curve characterised by a series of maxima at nearly equal intervals. We can now calculate the positions these maxima would occupy if the refractive index of nickel for electrons were unity. Substituting for d and θ their values 2·03 Å and 10° in the relationships, $\lambda = 12{\cdot}25/\sqrt{\text{V}} = 2d \cos \theta/\text{n}$, we find $\sqrt{\text{V}} = \text{n} \times 3{\cdot}06$. If the refractive index were unity, therefore, the maxima should be found at these values of $\sqrt{\text{V}}$. The positions of the maxima thus determined are shown in Fig. 3.

The observed maxima lie to the left of the calculated positions, the displacement decreasing, however, toward the higher orders. This is the type of displacement to be expected if the refractive index of the nickel for electrons is greater than unity. We can, in fact, use these displacements to calculate values of the refractive index. The more general form of the Bragg formula, applicable to the case in which the index is not unity, is :—

12·25

Using this formula and the data now available, it is found that the refractive index approaches unity as the speed of the electrons is increased. These results indicate that the purely geometrical differences between the reflection and diffraction of X-rays on the one hand, and of electrons on the other, disappear for electrons of high speed.

Evidence of refraction of electron beams has also been found by Rupp,[*] using rather low-speed electrons and thin films of polycrystalline metal. The diameters of the diffraction rings, observed in these experiments, differ slightly from those computed from the constants of the crystals and equation (1). Rupp ascribes these differences to refraction and uses their values to calculate the refractive indices of metals. The interpretation which Rupp gives to his observations has, however, been questioned by Thomson, who shows that refraction may be expected to produce a much smaller effect in experiments of the type made by Rupp and by himself than Rupp supposes.

5. Polarisation of the Waves. The close analogy between the properties of the waves associated with electrons, *etc.*, and electromagnetic waves has led investigators to search for polarisation in these waves. Davisson and Germer [†] reflected a beam of electrons successively from the faces of two nickel crystals, the angle of incidence at each reflection being 45°. The twice reflected beam was received in a Faraday box collector, and its intensity measured as the second reflector and the collector were rotated about the beam proceeding from the first crystal to the second one. If the electron waves are polarised by reflection, we should expect the current entering the collector to be a maximum when the planes of incidence of the two reflections are parallel, and a minimum when they are at right angles. The result found was that within the limits of uncertainty—about 0·5 per cent.—the current of electrons which survives the two reflections without loss of energy is independent of the azimuth of the second reflector. This result is in accord with a prediction made by Darwin, who has used Dirac's equations of the electron in considering the question of polarisation.

---

[*] *Ann. d. Phys.*, **1**, 773 (1929).

[†] *Loc. cit.*

Similar tests have been made by Joffre and Arsénieva * with polycrystalline targets of various materials, and Wolf † has tested for polarisation by reflection in a magnetic field. In both cases the results were negative.

On the whole the polarisation of the waves appears doubtful at present, but investigations are still in progress.

6. The Applications of Electronic Diffraction. Electron diffraction opens new possibilities for the examination of surface structure, and in this respect electrons have two advantages over X-rays. They penetrate less deeply, and the interaction between the electrons and the atoms of the experimental body is more intimate than that occurring in the case of X-rays. Germer ‡ and Rupp § found that the effect of allowing gas to come into contact with a nickel surface was to diminish the intensity of the diffraction maxima, due to layers of gas molecules covering the surface. From his results Germer concluded that the gas atoms form a single layer arranged like the atoms of the crystal, but with a double separation, and situated at a depth of 3Å below the first layer of nickel atoms. Rupp's experiments indicate that a layer of hydrogen gas on nickel undergoes a change during the course of time. He describes the process as a " surface loosening." There was no interaction between argon and nickel, but results were obtained in the case of hydrogen on other metals which resembled those with hydrogen on nickel. In other experiments a stream of electrons was generated by an incandescent wire and allowed to fall at a definite angle on to the surface of the crystal. The reflected electrons were measured, and the determination was repeated for the same surface upon which hydrogen, nitrogen and hydrogen sulphide had been adsorbed. The crystals used were single nickel crystals and pure iron, and the method was utilised to show the effect of nickel and iron as catalysts in the formation of ammonia.

---

* *Comptes Rendus*, **188**, 152 (1929).
† *Zeits. f. Phys.*, **52**, 314 (1928).
‡ *Ibid.*, **54**, 408 (1929).
§ *Ann. d. Phys.*, **5**, 453 (1930).

Thomson * has used electron diffraction to investigate surface layers of unknown composition. The nature of the patterns produced enables the crystalline structure of the surface to be determined. Polished and etched metals gave no pattern, nor did electro-deposited gold, or copper. It seems that almost any smooth surface, which has recently undergone chemical change, will give a diffraction pattern corresponding to the new crystal structure. Single crystals of calcite, galena and rock salt gave diffraction patterns of spots.

Boas and Rupp † utilised slow electrons for electron diffraction by oxygen-coated tungsten. The oxygen layer on tungsten was found to have the properties attributed by Langmuir to a monomolecular layer of oxygen.

Bühl and Rupp ‡ have shown that reproducible interference patterns are produced when electrons are reflected from oil surfaces.

The diffraction of electrons has been rendered visible on a fluorescent screen when such diffraction is effected by transmission through microcrystalline powders. Dauvillier has extended this method to thin films of organic materials and used it for their structural analysis, but the method is only applicable if the films are extremely thin, and do not sensibly absorb the electrons. The results show the possibility of the method for analysis of colloidal or fibrous materials, electronic analysis of this character permitting the study of a single microcrystal.

Another interesting problem connected with electron waves is that of the relative intensities of the various beams constituting the electron diffraction pattern. The study of intensities in X-ray diffraction patterns enables us to infer the distribution of electron

---

* *Proc. Roy. Soc., A.*, **128**, 649 (1930); *Journ. Sci. Inst.*, **8**, 173 (1931).
† *Ann. d. Phys.*, **7**, 983 (1931).
‡ *Zeits. f. Phys.*, **67**, 572 (1931)

charge within the unit cell of the crystal, and the like analysis in the case of electrons should enable us to infer the distribution of electrostatic potential. A theoretical basis for the interpretation of results of this kind has been suggested by Bethe.*

7. The Wave Characteristics of Free Atoms and Molecules. Experiments designed to show the wave characteristics of free atoms and molecules have been tried by several investigators. Ellett and Olson † reflected cadmium and mercury atoms from crystals of rock salt and found specular reflection. This might be regarded as the zero order diffraction beam, but no higher orders were found. Knauer and Stern ‡ reflected hydrogen and helium molecules from polished surfaces of steel and glass, and detected regular reflection at very small angles, as would have been expected if the phenomenon were that of the reflection of waves of wave-length, $\lambda = \frac{h}{mv}$, and the surface were rough to the order of 10^{-5} cm. These same molecules were found to be specularly reflected from cleavage surfaces of rock salt.

Johnson § reflected monatomic hydrogen from rock salt crystals and observed a sharply defined specular beam, but it was surrounded by such an intense diffuse background, arising, for the most part, from atoms having a cosine distribution, that it could not be said with certainty whether diffraction bands were, or were not, present.

Recently, Estermann and Stern || have investigated the reflection of helium and hydrogen from NaCl and LiF crystals, and found diffraction bands from the cross grating formed by the rows of similar ions on the surface of the crystal. The positions of the maxima of these bands were in practically complete agreement with the angles calculated from the first order diffraction of the most probable wave-length. Johnson ¶, also, in later experiments has obtained diffraction effects with atomic hydrogen, using crystals of LiF, thus providing further proof of the wave character of a beam of atoms.

---

* *Ann. d. Phys.*, **87,** 55 (1928).
† *Phys. Rev.*, **31,** 643 (1927).
‡ *Zeits. f. Phys.*, **53,** 779 (1929).
§ *Journ. Frank. Inst.*, **206,** 301 (1928).
|| *Zeits. f. Phys.*, **61,** 95 (1930).
¶ *Journ. Frank. Inst.*, **210,** 135 (1930) ; *Phys. Rev.*, **37,** 847 (1931).

Ellett, Olson and Zahl * found that beams of mercury, cadmium and arsenic atoms, incident upon clean cleavage surfaces of rock salt, give rise to specularly reflected beams. A beam specularly reflected from a first crystal is specularly reflected at a second one if incident upon it at the same angle at which reflection from the first takes place. If the angles are nearly equal there is still some specular reflection at the second crystal, but the intensity of the reflected beam decreases with increasing difference of angles and the incident beam is scattered at random. A beam of cadmium atoms, issuing from a boiler at 440° C. and striking a rock-salt crystal at an angle of 45°, gives rise to a reflected beam containing about 17 per cent. of the incident atoms. The intensity of the beams specularly reflected at 22·5° and 67·5° are in the ratio 1 : 1·38.

Taylor † reflected beams of lithium, potassium and cæsium atoms from crystals of sodium chloride and lithium fluoride. Although 0·01 per cent. of specular reflection could have been detected, no trace of such a reflection or diffraction was found.

Sawyer ‡ has studied the reflection of lithium ions from reflectors of platinum foil and nickel crystals deposited on tungsten foil. Readings were taken with both cold and hot reflectors. Superposed on a diffuse scattering of ions were two reflected beams. One was reflected nearly specularly, the angle of maximum reflection being independent of accelerating potential, but the other appeared only at voltages above 200 and was composed of ions most of which had retained 80 per cent. or more of their original energy. This beam was observed between the incident beam and the normal to the surface, at angles independent of the accelerating potential up to 700 volts. Sawyer suggests that this independence of angle on voltage forbids diffraction interpretations. A tentative explanation is to suppose specular reflection from the (110) planes of the nickel crystals, but it is not entirely satisfactory.

---

* *Phys. Rev.*, **34**, 493 (1929).

† *Ibid.*, **35**, 375 (1930).

‡ *Ibid.*, **35**, 1090 (1930).

8. The Existence of Waves. The question whether the waves, which we associate with particles, exist in the same manner that waves of light exist cannot be answered definitely, but various views have been expressed. Schrödinger suggested that the electron is a group of waves which he calls a " wave packet." It is difficult to understand how such a structure preserves its identity, and why it is not dispersed when it is diffracted by a crystal.

It has been suggested that the particle is a singularity in a wave, and this idea can be developed in the case of uniform motion, but it is impossible to generalise it. De Broglie also imagined that the particle and the wave were associated so that the former was guided by the latter, the wave acting as a pilot for the particle.

Wilson * supposes that a particle such as a photon, or electron, is practically identical with the group of waves associated with it, the energy and momentum being spread out over the group and not concentrated at a point. When the group is stopped, or absorbed, it contracts to small dimensions and so becomes a particle. It cannot be divided by reflection, or by passing through a small aperture in an opaque screen, but must be either all stopped or all transmitted. The group of waves must be regarded as a material entity, and the wave theory considered as an approximation, in so far as it now seems to require wave groups to be divided by reflection and other similar processes which do not involve any change of frequency.

The point of view which appears at present most satisfactory is one that supposes the wave to have no physical significance, ψ, a solution of the wave equation being a probability function. The patterns observed in the diffraction of electrons experiments are a representation of probabilities, the electrons falling according to definite probability laws into the places where they are seen in the patterns.

In conclusion, we have to admit that in both matter and radiation there exists a duality of wave and particle, the wave character being more obvious the lighter the particle. The nature of this duality is, as yet, by no means understood.

---

* *Phys. Rev.*, 35, 948 (1930).

BIBLIOGRAPHY

BIRTWISTLE. "The New Quantum Mechanics."
DE BROGLIE. "Introduction to Wave Mechanics."
CONDON and MORSE. "Quantum Mechanics."
DARROW. *Bell System Technical Journal*, 5, 64 (1927).
DIRAC. "Quantum Mechanics."
FLINT. "Wave Mechanics."
HEISENBERG. "The Physical Principles of the Quantum Theory.'
RUARK and UREY. "Atoms, Molecules and Quanta."
SCHRÖDINGER. "Wave Mechanics."
SOMMERFELD. "Wave Mechanics."
THOMSON, G. P. "The Wave Mechanics of Free Electrons."
THOMSON, J. J. "Beyond the Electron."

CHAPTER II

STATISTICAL MECHANICS

1. Introduction. A *macroscopic state* is one determined by quantities such as temperature and pressure, and can be measured by ordinary apparatus, whereas a *microscopic state* is one determined by the position and motion of all the parts of a substance, however small. A gas at a given temperature and pressure is in a definite macroscopic state, but its constituent molecules are in kinetic motion, so that its microscopic state is continually changing, and in a very short interval it includes an enormous number of different microscopic states, yet its macroscopic state can remain sensibly constant. This is explained by supposing that of all the possible microscopic states the vast majority correspond to values of the macroscopic quantities which differ inappreciably from the constant values. If the substance is not in a state of macroscopic equilibrium, its state changes until equilibrium is reached. Now the number of microscopic states, corresponding to any state differing appreciably from the macroscopic state, must be very small compared with the whole number of possible microscopic states, and the chance of the substance remaining an appreciable time in such a state must also be very small. Hence we infer that the substance changes to the equilibrium macroscopic state because the state corresponds to nearly all possible microscopic states, and this change involves an increase in the number of the latter states. Thus the equilibrium state is one for which the number of microscopic states is a maximum. From these considerations it is evident that the behaviour of a substance, if it consists of a very large number of individual particles, must be attributed to the *ensemble*, or assemblage as a whole, and the statistical method of investigation must be employed. In dealing with the assemblage by this method we do, in effect, fix the position of each particle, but with a certain latitude, and in the same way we assign a velocity to each, but again with a certain latitude. We use a function which represents the number of particles, assumed to be situated in each small element of volume, and the number assumed to have momenta within a small but definite range of momentum.

A function of this kind is known as a *distribution function.* It is usually written in the form :

$$dN = f(x, y, z, p_x, p_y, p_z,)\, dx\, dy\, dz\, dp_x\, dp_y\, dp_z,$$

where dN is the number of particles having co-ordinates between x and $x + dx$, *etc.*, and components of momentum between p_x and $p_x + dp_x$, *etc.* The product, $dx\ dy\ dz$, is a volume element in co-ordinate-space, and $dp_x\, dp_y\, dp_z$, a volume element in momentum-space, and we define the product $dx\ dy\ dz\ dp_x\ dp_y\ dp_z$ as a volume element in *phase-space*, so that f defines the distribution in this phase-space of six dimensions. In the case of photons the distribution in the co-ordinate-space is uniform and we can derive the distribution in the three-dimensional momentum-space.

2. State, or Phase, Space of a System. Suppose that the microscopic state of the system is defined by co-ordinates, $q_1, q_2, \ldots q_n$, and corresponding momenta, $p_1, p_2, \ldots p_n$, associated with these co-ordinates. We have $2n$ quantities which we may regard as the co-ordinates of a point in a space of $2n$ dimensions. This representative point will move along a closed curve, if the motion of the system is periodic, and will continue to do so as long as the energy of the system is constant. The space of $2n$ dimensions is called the *state*, or *phase*, *space of the system*, and if the state of the system is determined by its energy, the motion of the point round the curve does not involve a change in the state of the system.

If we have a large number N of such similar systems, and represent the state of each one in the $2n$-dimensional space by a representative point, the N points will describe curves in the space. The microscopic state of the *ensemble* can be regarded as determined by the energy distribution among the N systems, and we can imagine surfaces, or regions, in the state-space which are characterised by constant energy content. All systems, having the same energy, will thus have representative points moving on the same surface. From classical dynamics we should expect an infinite number of such regions, or surfaces, but, according to the quantum theory, only certain definite values of the energy of a system are permitted, and, therefore, on this theory, the number of surfaces would be limited. Thus the state-space will be divided into finite regions.

A change in the energy of one of the systems is represented by its point jumping from one surface to another, the two surfaces corresponding to the two values of the energy of the system. The point cannot occupy positions intermediate between surfaces. These jumps are attributed to actions occurring between the systems, or between the systems and radiation energy which an *ensemble* of atoms always shows.

3. The New Statistics. The basis of classical statistics is that if particles in space have identities, there are different ways of arranging the particles in the same distribution. One starts with an arrangement compatible with the prescribed distribution, *e.g.*, N_1 identical particles in one group, N_2 in another, *etc.*, and then obtains all the other arrangements by interchanging particles *ad libitum* among the groups, every one of the latter always containing the same number as it had at first.

When classical statistics is applied to an assembly of particles for which the relation between energy, ϵ, and momentum, p, is $\epsilon = cp$, as it is for radiation, *i.e.*, photons, instead of $\epsilon = p^2/2m$, as for mass particles, m being the mass of the particle, the energy distribution predicted is entirely different from that determined experimentally.

In the new statistics Bose * and Einstein † consider a volume V of a monatomic gas, and assume that corresponding to each of the atoms in the volume, there is drawn from a common origin a vector whose components are the three components p_x, p_y, p_z, of its momentum p_s. Since the state of each atom is defined by its co-ordinates (x, y, z) and momentum p_s, the volume of the phase-space containing momenta in the range p_s—p_s+dp_s is

---

* *Zeits. f. Phys.*, **26**, 178 (1924).

† *Sitz. Preuss. Akad. Wiss.*, **22**, 261 (1924).

$$\iiiint\!\!\iint dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

$$V \iiint dp_x\, dp_y\, dp_z, \text{ or, } V \cdot 4\pi\, p_s \qquad (1)$$

Introducing Planck's elementary quantum of energy, h, we may divide the phase-space into *cells* of volume h^3, so that the number of cells corresponding to the momentum range dp_s is :

and each possible energy state corresponds to a unit cell of volume h^3/V in this momentum-space.

Since the kinetic energy, ϵ, of the atom is given by $\epsilon = p^2/2m$, the number of possible energy states, Q, or cells, within the energy range ϵ and $\epsilon + d\epsilon$ is given by :

$$Q(\epsilon, \epsilon + d\epsilon) = \frac{V}{h^3}\, 2\pi(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}d\epsilon \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

Bose and Einstein assume that atoms can be associated with each unit cell of volume h^3/V. On the other hand, the statistics put forward by Fermi * and by Dirac,† although involving the same fundamental assumptions as those of Bose, postulate that the number of atoms associated with a given unit cell can only be 1, or 0, and that either number is equally probable. At higher temperatures, where the momenta are large, there is practically no restriction placed on the possible momenta. At low temperatures the cells near the origin of the momentum-space are nearly all filled, and there is a very distinct limitation on the possible momenta. At absolute zero all the cells nearest the origin are filled, but there is still a very definite energy, or zero-point energy in the gas. The latter is then said to be completely *degenerate*, a state which will now be more fully described.

An ideal gas may be defined as one which follows the equation :

$$p =$$

---

* *Zeits. f. Phys.*, **36, 902 (1926).**

† *Proc. Roy Soc., A.*, **112, 661 (1926).**

where p is the pressure, n, the number of molecules per c.c. and k, Boltzmann's constant. Any actual gas departs from this law owing to the finite size of its molecules and the forces of attraction and repulsion between them. For many years, however, it has seemed probable that even a gas which had no imperfection in this sense would nevertheless still show a departure from the law at high pressure and low temperature, either or both. In statistical mechanics this accompanies a departure from Maxwellian distribution of molecular velocities, and is the degeneracy of a gas.

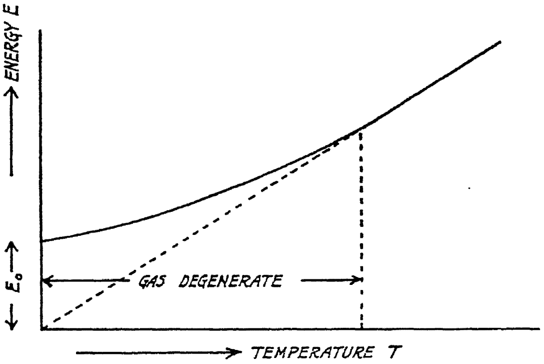


FIG. 6.—Relation between energy and temperature of a degenerate gas.

The full line in Fig. 6 shows the relation between energy and temperature of a degenerate gas. The dotted part extending through the origin shows the relation in a non-degenerate gas. E_0 is termed the *zero-point energy*, or *nul energy*.

As shown later the criterion of degeneracy is :

$$n$$

where n is now the number of atoms * per unit volume and m, the mass of an atom. Hence the temperature at which degeneracy first becomes felt varies as $n^{\frac{2}{3}}/m$. It is about 5° K. (absolute) for helium gas, and so if we imagine a gas consisting entirely of free electrons, degeneracy would be complete at 36,000° K., for the same number of electrons as helium atoms per unit volume.

---

* The gas is assumed to be monatomic.

4. The Distribution Function in a Degenerate Gas. Fermi examined the way in which the energy E of a gas partitions itself among N atoms in the following manner. Let Q_s be the number of energy states (cells) between ϵ_s and $\epsilon_s + d\epsilon_s$, and let N_s be the number of atoms distributed among these states. Then, according to Fermi's postulate,

$$N_s \leq Q_s. \qquad (3)$$

In addition,

$$N = \sum_s N_s\,; \quad E = \sum_s N_s \epsilon_s \qquad (4)$$

The number of ways in which the N_s atoms can be distributed under these conditions among the Q_s states is :

$$\frac{Q_s\,!}{N_s\,!\,(Q_s - N_s)\,!},$$

and the number of ways, **W**, in which the N atoms can be distributed among all the states is given by :

$$\mathbf{W} = \prod_s \frac{Q_s\,!}{N_s\,!\,(Q_s - N_s)\,!}. \qquad (5)$$

Using Stirling's theorem,

$$\log \mathbf{W} = -\sum_s \left[N_s \log \frac{N_s}{Q_s - N_s} + Q_s \log \frac{Q_s - N_s}{Q_s} \right]. \qquad (6)$$

Now the entropy of the gas, ϕ, is given by :

$$\phi = k \log \mathbf{W},$$

and in the actual distribution, N and E must be stationary and **W**, a maximum. Thus from equation (6),

$$\delta (\log \mathbf{W}) = \sum_s \left(\log \frac{Q_s - N_s}{N_s} \right) \delta N_s = 0.$$

Also, $$\sum_s \delta N_s = 0\,; \quad \sum_s \epsilon_s\, \delta N_s = 0.$$

Using undetermined multipliers :

$$\sum_s \left[\log \frac{Q_s - N_s}{N_s} - \alpha - \beta \epsilon_s \right] \delta N_s = 0,$$

where α and β are arbitrary coefficients. If this is true whatever the value of δN_s, then we must have,

$$\log \frac{Q_s - N_s}{N_s} - \alpha - \beta\epsilon_s = 0,$$

or,

$$N_s = \frac{Q_s}{e^{\alpha + \beta\epsilon_s} + 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In addition, we have,

$$N = \sum_0^\infty \frac{Q_s}{e^{\alpha + \beta\epsilon_s} + 1}\,; \quad E = \sum_0^\infty \frac{Q_s\epsilon_s}{e^{\alpha + \beta\epsilon_s} + 1} \quad . \quad . \quad (8)$$

Hence combining equations (2) and (7),

$$N_s \equiv N(\epsilon, \epsilon + d\epsilon) = \frac{V}{h^3} 2\pi\,(2m)^{\frac{3}{2}} \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\alpha + \beta\epsilon} + 1} \equiv F(\epsilon)\ . \quad (9)$$

At low densities and for large values of ϵ this should agree with the Maxwellian distribution, which may be written in the form :

$$\frac{K\epsilon\, d\epsilon}{e^{\epsilon/kT}},$$

where K is a constant. This agreement holds if $\beta = 1/kT$.

We now proceed to evaluate α. Since $N = \sum_0^\infty N_s$ and $E = \sum_0^\infty \epsilon_s N_s$, we have from equation (9),

$$N = \frac{V}{h^3} 2\pi(2m)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon\, k^{\frac{1}{2}}\, d\epsilon}{\epsilon^{\alpha + \epsilon/kT} + 1} \quad . \quad . \quad . \quad . \quad (10)$$

and

$$E = \frac{V}{h^3} 2\pi(2m)^{\frac{3}{2}} \int^\infty \frac{\epsilon^{\frac{3}{2}} d\epsilon}{e^{\alpha + \epsilon/kT} + 1} \quad . \quad . \quad . \quad . \quad (11)$$

Put $\epsilon/kT = x$, and,

$$\mathrm{F}\,(\alpha) = \frac{2}{\sqrt{\pi}} \int^\infty \frac{x^{\frac{1}{2}} dx}{e^{\alpha + x} + 1} \quad . \quad . \quad . \quad . \quad (12)$$

$$\mathrm{G}\,(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{\frac{3}{2}} dx}{e^{\alpha + x} + 1} \quad . \quad . \quad . \quad . \quad (13)$$

Then instead of equations (10) and (11) we get :

$$N = \frac{V(2\pi mkT)^{\frac{3}{2}}}{h^3} \,.\, \mathrm{F}(\alpha), \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

and
$$E = \frac{3}{2} VkT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \mathrm{G}(\alpha) = \frac{3}{2} NkT \frac{\mathrm{G}(\alpha)}{\mathrm{F}(\alpha)} \quad . \quad . \quad . \qquad (15)$$

For very large positive values of α, corresponding to densities and temperatures where the gas is not degenerate, we can obtain F(α) and G(α) in the form of series, thus :

$$\mathrm{F}(\alpha) = e^{-\alpha} - \frac{e^{-2\alpha}}{2^{\frac{3}{2}}} + \frac{e^{-3\alpha}}{3^{\frac{3}{2}}} -, \quad . \quad . \quad . \quad . \quad . \qquad (16)$$

$$\mathrm{G}(\alpha) = e^{-\alpha} - \frac{e^{-2\alpha}}{2^{\frac{5}{2}}} + \frac{e^{-3\alpha}}{3^{\frac{5}{2}}} -, \quad . \quad . \quad . \quad . \quad . \qquad (17)$$

so that to a first approximation, $\mathrm{F}(\alpha) = \mathrm{G}(\alpha) = e^{-\alpha}$, and equations (14) and (15) reduce to :

$$\alpha = \log \left[\frac{V}{N} \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\right], \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

and
$$E = \frac{3}{2} NkT,$$

as in the classical statistics.

When α assumes large negative values, *i.e.*, at low temperatures, corresponding to strong degeneration, both F(α) and G(α) assume asymptotic forms, *viz.*,

$$\mathrm{F}(\alpha) = \frac{4}{3\sqrt{\pi}}(-\alpha)^{\frac{3}{2}}\left[1 + \frac{\pi^2}{8\alpha^2} + \dots\right] \quad . \quad . \quad . \qquad (19)$$

$$\mathrm{G}(\alpha) = \frac{8}{15\sqrt{\pi}}(-\alpha)^{\frac{5}{2}}\left[1 + \frac{5\pi^2}{8\alpha^2} + \dots\right] \quad . \quad . \quad . \qquad (20)$$

so that substituting for F(α) in equation (14),

$$\alpha = -\frac{1}{8}\left(\frac{6N}{\pi V}\right)^{\frac{2}{3}} \frac{h^2}{mkT}\left[1 - \frac{16\pi^2}{3}\left(\frac{\pi}{6} \cdot \frac{V}{N}\right)^{\frac{4}{3}} \frac{m^2k^2T^2}{h^4} + \dots\right]. \qquad (21)$$

Substituting these results in equation (15) we see that there is a nul-point energy, *i.e.*, the energy does not vanish at $T = 0$. The value of this nul-point energy, E_0, is given by :

$$\frac{E_0}{N} = \frac{3}{40}\left(\frac{6}{\pi}\right)^{\frac{2}{3}}\frac{h^2}{m}\left(\frac{N}{V}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

If we differentiate equation (15) with respect to T, we obtain the specific heat at constant volume C_v (per gram-atom),

$$C_v = \frac{L}{N}\frac{dE}{dT} = \left(\frac{4\pi}{3}\right)^{\frac{2}{3}}\frac{\pi^2 Lmk^2 T}{h^2 n^{\frac{2}{3}}} \quad . \quad . \quad . \quad . \quad . \qquad (23)$$

where L is the number of atoms per gram-atom, n being the number of atoms per c.c. Hence the specific heat is proportional to the absolute temperature and vanishes at the absolute zero in accordance with Nernst's Heat Theorem.

If α is large and positive, the distribution law, equation (10), differs little from the Maxwellian law. This is so for all ordinary gases, except at very low temperatures or very high pressures. The condition for proximity to, or large divergence from, the Maxwellian law is obtained from equation (18). Thus,

(I) α large and positive, *i.e.*, $\frac{V}{N} \qquad h^3 \qquad > 1$. The distribution is Maxwellian.

(II) α large and negative, *i.e.*, $\frac{V}{V}\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} < 1$. The distribution is non-Maxwellian.

The first condition is satisfied for ordinary gases at normal temperatures and pressures. When the second condition is satisfied we see from equation (7) that $N_s = Q_s$, approximately, and every cell is filled. The assembly is degenerate.

5. Comparison of the Statistics Theories. We may illustrate the essential difference between the three statistics by means of the following simple example.* Suppose that there are only two members of an *ensemble* and only two cells in the phase-space. The characteristic feature of the classical statistics is that each member is assumed to have an identity, and each is as likely to be in one cell as in another. There are thus four possible arrange-

---

*** See Lennard-Jones, *Proc. Phys***

ments as shown in Fig. 7, and each is to be counted in assigning a probability to the distribution. In the Bose-Einstein statistics, however, the members of the *ensemble* lose their identity, and attention is concentrated on the cell rather than on the individual members of the *ensemble*. In the figure, therefore, we represent the members by indistinguishable points. Each cell may have any number of points, and so the total number of possible arrangements is three. In the Fermi-Dirac statistics, on the other hand, not more than one representative point is to be in any one cell, with the result that in this simple case only one arrangement is possible. When there are a large number of cells, and comparatively few points to arrange in them, there is no essential difference between the three methods, because the likelihood of any cell containing more than one point is very small. It is when the number of points is comparable with the number of cells that the three methods lead to divergent results. Brillouin * has also given a method of discriminating between the three cases.

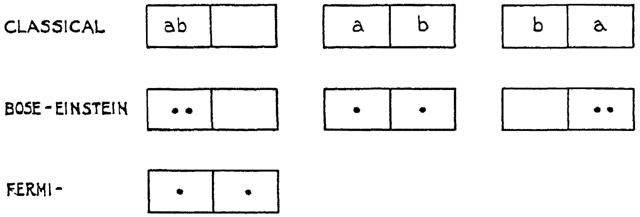


FIG. 7.—Comparison of statistics theories.

6. Application of Fermi-Dirac Statistics to the Electron Theory of Metals. The present view concerning the various properties of metals, such as specific heat, photo-electricity, thermo-electricity, *etc.*, is that all these properties can be explained if we conceive a piece of metal as a region containing free electrons and surrounded by a boundary-surface; these free electrons may be looked upon as forming a perfect gas, an idea which is tantamount to ignoring the atoms, to supposing the metal a vacuum inhabited by free electrons only. This is by no means a new idea, but in the past, when classical statistics was applied to the electron gas, it was found impossible to choose a value for the number of electrons per unit volume, n, which would predict values for the various properties of metals in agreement with the experimental ones. For example, if the value of n was assumed to be large, the predicted value of the specific heat was too large, while if n were reduced to meet this objection, other predictions were impaired. For these reasons the "electron gas" theory was discredited to some extent.

---

* *Comptes Rendus*, **184**, **589** (**1927**).

Sommerfeld,[*] however, has recently revived the electron theory of metals, based on a greatly simplified model of the interior of a metal as a region of uniform potential, positive relative to free space, so that work is required to extract an electron from rest in the metal to rest at infinity. The electrons, however, are not all at rest, but form practically a perfect gas, a gas, however, at such a concentration that they are almost tightly packed, and obey the Fermi-Dirac statistics. It is assumed that the number of free electrons per unit volume is equal to the number of atoms per unit volume. Thus, $\frac{N}{V}$ is of the order 10^{22}, or 10^{23}, per c.c., and we find that for $T = 300^0 K$,

$$\frac{V}{N}\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} = 2 \times 10^{-4}, \text{ approximately.}$$

In other words, α is large and negative and, therefore, according to the conditions set forth in Section 4, the distribution in the electron gas is non-Maxwellian, and the gas itself is degenerate. It is the small mass of the electron which differentiates it from ordinary gas atoms and leads to this result. One important consequence of this application of the new statistics is that the contribution of the electrons to the specific heat is negligibly small. This disposes of a well-known difficulty in the electron theory of metals, and constitutes one of the most striking successes of the new statistics. Sommerfeld calculates that the pressure exerted by the electrons is of the order 2×10^5 atmospheres.

---

[*] *Zeits. f. Phys.*, **47**, 1, 43 (1928).

7. Zero-point Energy and Specific Heat. If we are to attribute the phenomena connected with the flow of electricity in metals to the presence in the metal of a number of free electrons, of the order of 1 per atom, on the theory of the equipartition of energy the free electrons ought to share in the heat motions of the atoms, and, therefore, to reveal their presence in specific heat measurements. This they have failed to do. It is a well-known fact that metals obey, more or less, the law of Dulong and Petit and that the whole of the specific heat is accounted for as atomic heat. The application of the Fermi-Dirac statistics has accounted for this apparent contradiction. We have shown, previously, that an electron gas should show signs of becoming degenerate at temperatures of the order 36,000° C. At ordinary temperatures degeneration will be practically complete, and the average energy of the electrons will be very near the zero-point energy.

The statistics developed have referred to atoms which possess no energy beyond their energy of translation. Goudsmit and Uhlenbeck,* however, supposed the electron to be spinning about an axis like a top or planet, so that the spinning electron has energy of rotation as well as translational energy and, therefore, in a magnetic field will set itself with its axis of spin in the direction of the field. But its rotation may be in either of two directions about that axis. Since the angular momentum is perfectly definite in either case, the electron may exist in two, and only two, states, *i.e.*, it has what we may term statistical weight two. The natural extension of the Fermi-Dirac statistics to the case of the electron is to allow two electrons, one in each direction of spin, in each cell of the momentum space. This leads us to replace n by $n/2$ in the formula for the zero-point energy and for the specific heat.

On substituting numerical values in equation (22) we obtain for the zero-point energy of the electrons in sodium :

$$\frac{E_0}{N} \qquad \times 10^{-12} \text{ ergs.}$$

This is the energy which an electron would possess at 15,000° C.

---

e, 117, 264 (1926).

on the old equipartition of energy theory. The corresponding voltage is 2 volts. As for the specific heat we find on substituting numerical values in equation (23) that the contribution of the electrons at ordinary temperatures is of the order of 1/100th of that of the atoms. Hence we should not expect to detect it in any specific heat measurements at ordinary temperatures.

8. The Fermi Distribution for an Electron Gas. The distribution function, $F(\epsilon)$, for an electron gas is obtained from equations (9) and (21), remembering that owing to the spin of the electron

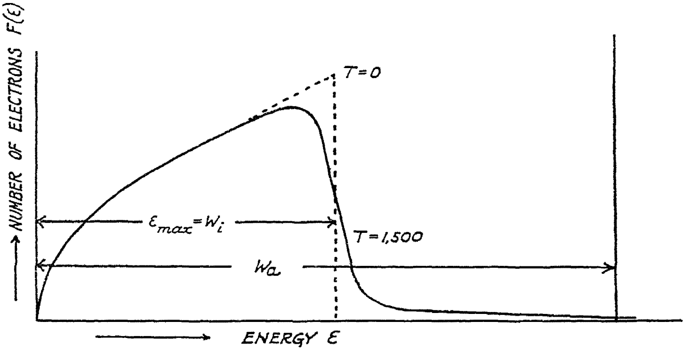


FIG. 8.—Distribution of energy among electrons in a metal. (Fermi-Dirac statistics.)

N/V or n, the number of electrons per unit volume, becomes $n/2$. Thus,

$$V \qquad \epsilon^{\frac{1}{2}}\,d\epsilon$$

where

$$6N$$

When T is zero, the exponential term in the expression for $F(\epsilon)$ is either infinity or zero, according as the variable ϵ is greater, or less, than W_i. Hence the density of the electrons in phase-space is zero for all values of the energy greater than W_i. The corresponding speed, v_m, of the fastest electrons is obtained from $\frac{1}{2}mv_m{}^2 = W_i$ and, therefore, is given by the expression :

$$= \frac{h}{m}\left(\frac{3n}{8\pi}\right)^{\frac{1}{3}}.$$

No electrons of energy greater than W_i are present in the metal.

Plotted as a function of ϵ, the distribution function $F(\epsilon)$ in energy is at first a parabolic curve, convex upward, dropping to zero abruptly at $\epsilon = W_i$, Fig. 8, and thenceforth coinciding with the ϵ axis. As the temperature rises Sommerfeld has shown that the discontinuities in the curve are gradually rounded off. We may assume that a complete degeneration distribution exists even at room temperature. In practice, the values of W_i are large, *viz.*, 5·6 volts for silver, 5·7 for tungsten, 2·1 for potassium, and 3·2 for sodium. Thus in the case of silver, for example, the electrons are distributed throughout a range of energies extending from zero to 5·6 volts, whereas if they were distributed according to the Maxwellian law they would be distributed about a mean energy of, approximately, 0·02 volt. This example emphasises the difference between the old and new statistics as applied to an electron gas.

9. The Susceptibility of Metals. It is a well-known fact that many metals, especially the alkalis, exhibit only slight paramagnetic properties, and the susceptibility is practically independent of temperature. All attempts to construct a theory on classical lines have led to a variation of susceptibility with temperature. Recently, however, Pauli * has explained the observed facts on the assumption that the magnetic properties are due to free electrons in the metal, the electron possessing a magnetic moment by virtue of its spin. He deduces the following formula for the susceptibility per unit volume, χ_v, of the electron gas,

$$= 12\left(\frac{\pi}{3}\right)^{\frac{2}{3}}\frac{\mu^2 n^{\frac{1}{3}} m}{h^2} \text{ approximately,}$$

where μ is the magnetic moment of the electron due to its spin. Thus the susceptibility of the electron gas is constant and independent of the magnetising field. Substituting numerical values for the constants we obtain,

---

* *Zeits. f. Phys.*, **41**, 81 (1927).

$$\chi_v = 2{\cdot}209 \times 10^{-14}\, n^{\frac{1}{3}}.$$

The question arises whether the susceptibility of a metal is due entirely to the electron gas within it. The magnetisation of an ordinary paramagnetic metal is a threefold effect, involving the orientation of the electrons, the orientation of the atoms, and the alteration of the electron orbits in the atom which gives rise to diamagnetism. Spectroscopic data show that the magnetic moment of an alkali atom, with its valence electron removed, is zero, so that there remain the other effects, the diamagnetic effect increasing with atomic number.

Although the value of χ_v deduced above is for absolute zero, the susceptibility of the electron gas remains practically the same up to room temperatures, and it is known that the susceptibility of the alkali metals is independent of temperature, a fact which led Pauli to investigate the paramagnetism of the electron gas. If the latter were governed by classical statistics, the susceptibility of a metal would increase as the temperature decreased and attain very great values near the absolute zero.

Pauli has calculated the susceptibility of the electron gas in the alkali metals on the assumption that there is one free electron per atom. The calculated values agree as well as can be expected with the experimental results, but as shown in the following table there are large discrepancies between various observed values :—

Element.	Mass (Specific) Susceptibility × 10^6				
	Pauli (calculated).	Owen.*	Sucksmith.†	McLennan.‡	Lane.§
Li	—	0·50	—	—	—
Na	0·68	0·50	0·59	0·59	0·65
K	0·60	0·58	0·51	0·45	0·54
Rb	0·32	0·076	0·07	0·17	0·21
Cs	0·23	—1·0	—0·05	0·18	0·22

---

* *Ann. d. Phys.*, **37**, 657 (1912).
† *Phil. Mag.*, **2**, 21 (1926).
‡ *Proc. Roy. Soc., A.*, **116**, 468 (1927).
§ *Phil. Mag.*, **8**, 354 (1929) ; *Phys. Rev.*, **35**, 977 (1930).

An interesting feature is the wide divergence between the experimental and calculated values for rubidium, especially in view of the fact that the agreement between theory and experiment in the cases of sodium, potassium and cæsium is remarkably close. In this respect, then, rubidium seems to be anomalous.

The only factor in Pauli's formula which might conceivably be incorrect is n. In order to bring the theoretical value into agreement with the observed one it would be necessary to suppose that n is actually about one-third its present accepted value, or, rather, for some reason, only about one-third the number of free electrons per unit volume contribute to the paramagnetism. Of course, we should not expect very close agreement with the Pauli formula since the latter neglects certain factors which should contribute to the susceptibility, *viz.*: (1) the diamagnetic effect of the atom cores; (2) a possible diamagnetic induction effect of the free electrons. We are at present unable to make any definite statement about the magnitude of these effects since no satisfactory theory for them has appeared. Rosenfeld [*] has estimated the diamagnetic effect of the cores as a function of the lattice potential, but since only the order of this quantity is known, the correction appears rather uncertain. In any event no data whatever exist for the alkali metals.

The Pauli theory can only be considered as provisional, since in its present form it is quite unable to account for at least two important facts, namely, the observations of McLennan, Ruedy and Cohen [†] on the variation of susceptibility with orientation in single crystals of zinc and cadmium, and the observations of Lane [‡] on the sudden change in susceptibility in passing over from the solid to the liquid state in the case of cæsium.

The free electrons must interact to some extent, and in a complete theory this interaction must be taken into account.

McLennan's results show that the susceptibilities of the alkali metals are approximately constant from room temperature down to —190° C. At the melting point there is an abrupt but small decrease, and above, a gradual increase in the susceptibility with temperature.

---

[*] *Naturwiss.*, **17**, 49 (1929).

[†] *Proc. Roy. Soc., A.*, **121**, 9 (1928).

[‡] *Phil. Mag.*, **8**, 354 (1929).

10. Electrical Conduction. Sommerfeld has considered the whole electron theory of metals in the light of the new statistics, and obtained the following formula for the electrical conductivity, σ, of metals :—

$$\sigma = \frac{8\pi}{3} \frac{\mathrm{e}^2 l}{h} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}},$$

where l, the mean free path of the electrons, is assumed to be a function of their kinetic velocity, v.

The classical theory gives :

$$\begin{array}{ll} 4 & \mathrm{e}^2 l n \\ 3\ (2 & \end{array}$$

and experiment shows that σ is inversely proportional to T.

Houston * treated the electrons as waves in accordance with the views put forward in the previous chapter, the equivalent wavelength being about 5Å. Departing from the usual custom of considering encounters between electrons and atoms, he calculated the scattering of the electron waves by atomic centres, taking into account the heat motion of the atoms. He found, as a result, that the electrical conductivity varied inversely as the temperature at normal temperatures, and inversely as the square of the temperature at very low temperatures. Thus, his theory is in accord with facts at high temperatures, and indicates, what is the case, that there is a rapid increase in the conductivity at low temperatures, but this calculated increase is not as great as that found experimentally. In spite of this, however, the theory is more successful than any other in its interpretation of the dependence of electrical conductivity on temperature. It fails, as do all the others, to account for the phenomenon of *superconductivity*.

11. Thermal Conduction. Sommerfeld, adopting the Fermi distribution function, calculated the net rate of flow of kinetic energy, borne by electrons, through unit area perpendicular to the temperature gradient, and obtained the following expression :

---

* *Zeits. f. Phys.*, **48**, 449 (1928).

$$8\pi^3 \cdot \frac{lk^2T}{h} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \frac{dT}{dx},$$

where the coefficient of dT/dx is, by definition, the thermal conductivity, κ. Thus,

$$\kappa = \frac{8\pi^3}{9} \cdot \frac{lk^2T}{h} \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}},$$

whereas the classical theory gives :

$$\kappa = \frac{8}{3} \frac{lnk^{\frac{3}{2}}T^{\frac{1}{2}}}{(2\pi m)^{\frac{1}{2}}}.$$

Neither formula agrees with the experimental fact that κ is independent of temperature, although both, like those for σ, involve the more or less disposable constants, n and l.

For the ratio of thermal to electrical conductivity, the old statistics and the new give expressions involving nothing but T, and the ratio of the universal constants k and **e**. They differ only by a small numerical factor, thus :

$\frac{\kappa}{\sigma} = 2(k/\mathbf{e})^2T.$ Classical statistics.

$\frac{\kappa}{\sigma} = \frac{\pi^2}{3}(k/\mathbf{e})^2T.$ Fermi statistics.

$\frac{\kappa}{\sigma} = (3 \ldots 3{\cdot}5)(k/\mathbf{e})^2T.$ Experimental results.

The numerical factor in the ratio $\frac{\kappa}{\sigma}$ is closer, according to the new statistics, to the experimental value than that of any previous theoretical formula. For many metals the value of κ/σ at 291° absolute is $7{\cdot}11 \times 10^{-11}$, whereas the value according to Sommerfeld's calculation is $7{\cdot}1 \times 10^{-11}$. This agreement seems too satisfactory and may be partly accidental. Both the classical and Sommerfeld's theories require that the ratio be proportional to T, and this requirement is satisfied over wide temperature ranges. At low temperatures, however, there is marked divergence between calculated and experimental values.

12. Potential Difference. If the number of electrons per unit volume in a metal varies from point to point, we should expect the electrons to diffuse from regions of higher to regions of lower density, unless they are impeded by some force. There is such a force, X, *i.e.*, an internal electric field, which prevents this diffusion, and Sommerfeld * has shown that the acceleration, $\mathrm{e}X/m$ of an electron, which this force produces, is given by :

$$\frac{\mathrm{e}X}{m} = \frac{h^2}{3m^2}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}} n^{-\frac{1}{3}} \frac{dn}{dx}.$$

Integrating,

$$-X(x_A - x_B) = (\mathrm{V}_A - \mathrm{V}_B) = \frac{h^2}{2m\mathrm{e}}\left[\left(\frac{3n_A}{8\pi}\right)^{\frac{2}{3}} - \left(\frac{3n_B}{8\pi}\right)^{\frac{2}{3}}\right], \quad (26)$$

or, from equation (25).

$$\mathrm{V}_A - \mathrm{V}_B = \frac{1}{\mathrm{e}}\left[(W_i)_A - (W_i)_B\right], \quad . \quad . \quad . \quad (27)$$

where V_A is the potential at x_A and V_B at x_B. Thus, if at any two points, A and B, the number of electrons per unit volume are n_A and n_B, respectively, there is an internal potential difference equal to $\mathrm{V}_A - \mathrm{V}_B$ between these two points.

We may obtain this result in a simple manner as follows : The maximum energy possessed by the electrons at the point A is, from equation (25),

$$\frac{h^2}{2m}\left(\frac{3n_A}{8\pi}\right)^{\frac{2}{3}},$$

and a similar expression represents the maximum energy of the electrons at B, although, as Fowler † has pointed out, $\epsilon_{\mathrm{max.}}$ is not an absolute maximum, but simply a value which is exceeded only by a very small proportion of the electrons. Hence, there will be a change in the energy of an electron, possessing this maximum energy, when the electron is removed from A to B, and equating this change to the electrical work done, *viz.*, $e(V_A - V_B)$, equation (26) follows immediately.

---

* *Loc. cit.*

† *Proc. Roy. Soc., A.*, **118**, 229 (1928).

Let us now imagine two pieces of different metals welded together, and that the process of welding does not alter the concentration of the electrons in either metal at points removed from the weld. If A and B, Fig. 9, are two such points, A in one metal and B in the other, then the internal, or intrinsic, potential difference between A and B is given by equation (26). This presupposes that the number of electrons per unit volume is not the same in the two metals, a supposition that is justified if the number of electrons is equal to the number of atoms per unit volume.

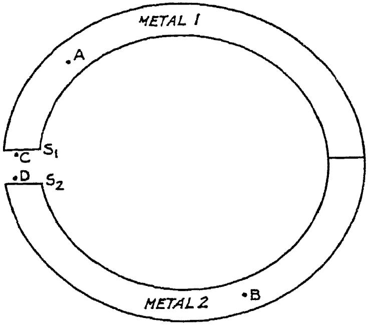


FIG. 9.—Intrinsic potential difference and contact potential difference.

The classical statistics also predicts an internal potential difference, but the value is different from that obtained according to the Fermi-Dirac statistics.

Although it is impossible to measure this potential difference, thermo-electric phenomena indicate that it exists. In the case of silver and potassium, for example, if we assume that in each unit volume of these metals there are as many electrons as atoms, and if this state of affairs still persists when the metals are joined, then between the interiors of the metals, across the junction, there must be, according to the new statistics, a potential difference of 4·2 volts, with potassium negative. The classical theory gives a result, 0·04 volt, which is considerably lower.

This intrinsic potential difference is not a measure of the contact potential difference, the so-called *Volta-effect*, between a pair of metals, as may be shown in the following way.

The electrons belonging to the interior electron gas will bombard the boundary-surface of the metal, and if they possess an energy component, $\frac{1}{2}mv_0^2$, normal to the surface greater than a constant, W_a, they will escape from the metal. Hence, the condition for escape is :—

$$\tfrac{1}{2}mv_0^2 = W_a.$$

W_a is called the *external work function.* It is the work required to overcome the attraction of the positive charges in the metal for the electrons. It corresponds, therefore, to the energy required to remove an electron, initially at rest, from the metal, or it may be regarded as a retarding potential fall at the metal surface. Thus, if W represents the work required to remove a free electron from a point in a metal, where the number of electrons per unit volume is n_A, into the space outside, we have,

$$W = W_a - \frac{\quad}{2m}\left(\frac{3n_A}{8\pi}\right)^{\frac{2}{3}},$$

or, from equation (25),

Now consider two points, C and D, Fig. 9, close to two metals of which one set of junctions have been welded together. W_1, the work done in removing an electron from A to C, *viâ* the surface S_1, is :—

$$W_1 = (W_a)_1 - (W_i)_A,$$

where the suffix 1 refers to the first metal and suffix A to the point A. The work, W_2, required to remove an electron from A, *viâ* the weld and the surface S_2 to D is :—

$$W_2 = (W_a)_2 - (W_i)_A + (W_i)_A - (W_i)_B.$$

Hence the potential difference between C and D is :—

$$\mathrm{e}\,(W_1 - W_2) = \frac{1}{\mathrm{e}}\left\{[(W_a)_1 - (W_a)_2] - [(W_i)_A \qquad\right\} \qquad (28)$$

and this is the contact potential difference between the two metals. It is quite different from the internal potential difference, equation (27).

We have assumed that there is a sharp potential fall at the metal surface, and beyond the surface is the equipotential region of outer space. Several investigators,* however, have conceived the region beyond the surface to be one in which there is an electric field, the strength of which is a function of the distance from the surface. If this is so, W_a is the integral of this field strength from the surface to infinity.

---

* See Fowler and Nordheim, *Proc. Roy. Soc.*, *A*, **119**, 173 (1928) ; Nordheim, *Phys. Zeits.*, **30**, 177 (1929) ; Fürth, *Zeits. f. Phys.*, **68**, 735 (1931).

The measurement of the contact potential difference between two metallic surfaces is a subject which has attracted the attention of experimenters for many years. Unfortunately, the values obtained have been most inconsistent, chiefly on account of the great difficulty of keeping metal surfaces free from contaminating films. The great amount of experimental work with thermionic tubes during the last fifteen years has emphasised the difficulty of keeping hot filaments free from surface contamination, and when the surfaces used are cold, as is usually the case in contact potential, this difficulty is increased.

Langmuir and Kingdon * made contact potential measurements between filamentary electrodes, which could be easily cleaned by heating. Moreover, by working with adsorbed films, the surface of a single filament could be brought into different states, and the contact potential differences between these states determined. The method of preparation of the surfaces was as follows : The tungsten (W) surface was prepared by flashing for a short time at a high temperature. By letting oxygen come into contact with the cleaned cold filament, a tungsten surface with adsorbed oxygen (OW) was prepared. A cæsium-tungsten surface (CsW) was similarly prepared by letting cæsium vapour deposit on the cleaned, cold filament. For a cæsium-oxygen-tungsten surface (CsOW) an oxygen layer was first formed on the cleaned filament, sometimes by adsorption with the filament cold, and sometimes by heating the filament for 1 second at about 2,000° K. in a low pressure of oxygen. Cæsium was then allowed to deposit on this surface.

The average values of contact potential were :

CsOW — W : 3·1 volts. ThW — W : 1·46 volts.

CsW — W : 2·8 ,, W — OW : 0·8 ,,

The ThW symbol refers to a thorium film on the tungsten filament.

---

* *Phys. Rev.*, **34**, 129 (1929).

In each case the surface on the left is positive to the one on the right.

The contact potential differences, ΔV, are connected with the thermionic constants for the various surfaces by the relation * :

$$\Delta V = \phi_1 - \phi_2 + (T/11600) \log (A_2/A_1),$$

where ϕ_1 and ϕ_2 are the work functions of the two surfaces, expressed in volts, T, the temperature, and A_1 and A_2 are the values of the A constant of the thermionic emission equation. The observed values of the contact potential between various surfaces, together with the values calculated by means of this equation, are shown below :—

Surfaces.	ΔV (calculated) volts.	ΔV (observed) volts.
ThW—W	1·81	1·46
CsOW—W	3·55	3·1
W—OW	4·12	0·8

The contact potential differences were calculated for a temperature of 300° K., since the filaments were not heated. The agreement is not good, and in no case was there any indication of a contact potential difference of 4-volts between tungsten and oxidised tungsten. The disagreement between the calculated and experimental values may be due to the fact that the electron emission constants, used in the calculation, were determined at elevated temperatures, whereas the contact potential differences were calculated for room temperature.

Kösters † has also recently measured the contact potential of tungsten, tantalum, molybdenum, nickel, copper and chromium in high vacuum, the tube containing the metals being cooled in liquid air. He found that heating the metals to remove the occluded and adsorbed gases caused first an increase, and then a decrease of the surface potential, but the total variation was not more than a few tenths of a volt, and the final value remained

---

* Richardson, " Emission of Electricity from Hot Bodies," p. 41 (1921).
† *Zeits. f. Phys.*, **66**, 807 (1930).

constant for many hours. With tungsten, tantalum, and molybdenum the potentials were constant and readily reproducible, and were in quantitative agreement with the work of electronic separation, as calculated from thermionic emission experiments. Kösters concludes from this that the contact potential of a substance is a true constant and not merely a result of the condition of the surface. Other measurements with nickel—copper and chromium—tungsten were less satisfactory.

Recently, Dubois* in measuring the contact potential has found that the metal shows at first, for heating at moderate temperatures, a variation of potential in the positive sense, called the positive variation. When heated at higher temperatures, there is then produced a variation of potential in the inverse sense, called the negative variation. Also there occurs after each heating, in the positive sense, a variation of potential with time. The first two variations are due to the driving off of impurities, of which the two principal are probably oxygen and water vapour. Traces of alkaline salt can render a metal more electro-positive. The variation with time corresponds probably to a diminution of the density of the electronic emission of the pure metal.

Polednik † has determined the contact potential of various

Metal.	Contact Potential in Volts with Respect to	
	Quartz.	Glass.
Platinum	+ 2·22	+ 1·15
Iron	+ 1·99	+ 1·15
Copper	+ 1·60	+ 0·58
Gold	+ 1·60	+ 0·58
Silver	+ 1·42	+ 0·58
Aluminium	+ 0·93	+ 0·14
Magnesium	+ 0·93	+ 0·14
Zinc	+ 0·45	— 0·29
Lead	+ 0·16	— 0·60
Tin	— 0·30	— 1·14

---

* *Ann. de Phys.*, **14**, 627 (1930).

† *Zeits. f. Phys.*, **66**, 619 (1930).

metals with respect to quartz and glass in a vacuum of the order of 10^{-5} mm. of mercury. The results, which can be successfully repeated to a considerable degree of accuracy, are exhibited in the table above.

13. Thermionics. The emission of electricity from hot bodies has been investigated, theoretically, by Sommerfeld who deduced the equation for emission by means of the Fermi-Dirac distribution function for an electron gas. It is assumed that the thermionic current is produced by all those electrons which strike the boundary-surface of the metal with velocities, such that the components normal to the surface, v, are greater than those corresponding to the relation :

$$\tfrac{1}{2}mv^2 > W_a.$$

Denoting by $F(\epsilon_N)d\epsilon_N$ the number of electrons having normal energies between ϵ_N and $\epsilon_N + d\epsilon_N$ which strike unit area per unit time, the relation deduced is of the form :

$$F(\epsilon_N) = \frac{4\pi m}{h^3} kT \log \left(1 + e^{-(\epsilon_N - W_i)/kT}\right).$$

$$\text{Hence} \quad F(\epsilon_N) = \frac{4\pi m}{h^3} (W_i - \epsilon_N) \text{ for } \frac{\epsilon_N - W_i}{kT} \ll 0,$$

$$= \frac{4\pi m}{h^3} kT, \text{ approximately, for } \epsilon_N \simeq W_i,$$

$$= \frac{4\pi m}{h^3} kTe^{-(\epsilon_N - W_i)/kT} \text{ for } \frac{\epsilon_N - W_i}{kT} \gg 0.$$

For values of $\epsilon_N > W_i$ the distribution curve follows the Maxwellian distribution law, which is in agreement with observations on the velocity distribution for the electrons emitted from a hot cathode.

By forming the integral of $F(\epsilon_N)d\epsilon_N$ for the limits $v = v_0$ to $v = \infty$, and for the limits of u and w the values 0 and ∞, where u and w are the other velocity components, the electron current, per unit area, I, is obtained in the form :

$$I = \qquad e^{-(W_a -} \tag{29}$$

where g is a factor to which has been assigned the value 2 by Fowler * on the basis of the hypothesis of electron spin.

Assuming the Maxwellian distribution law for the electrons within the metal, I is given by :

$$I = \frac{\mathrm{e}n}{(2\pi m)^{\frac{1}{2}}}(kT)^{\frac{1}{2}}\,e^{-W_a/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Richardson † derived an equation of the form :

$$I = AT^2e^{-b_0/T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

on the basis of the quantum theory, where the value of A has been deduced by Dushman ‡ to be equal to

$$\frac{2\pi \mathrm{e} m k^2}{h^3}.$$

Comparing equations (29) and (31) we see that they differ in two respects,

(1) The presence of the factor g.

(2) The substitution in the exponential factor of the classical b_0 by $(W_a - W_i)/k$.

However, the fact that both classical thermodynamics and the Fermi-Dirac statistics lead to the same value for the coefficient of T^2, except for the factor g, is extremely significant. Apparently the statistical method does not indicate any reason for deviations in the observed value of this coefficient from the theoretical value.

According to Sommerfeld's derivation of the equation for emission, it is assumed that all the electrons in the metal reaching the inner wall with normal energy greater than W_a are transmitted. But Nordheim § has shown from considerations based on the application of wave mechanics, that, in general, some of the electrons will be reflected at the boundary. The transmission coefficient is a function of the normal kinetic energy ϵ_N. Accordingly, Fowler || suggested that,

$$I = (1 - r)\frac{2\pi \mathrm{e} m g}{h^3}(kT)^2e^{-(W_a - W_i)/kT}, \quad . \quad . \quad . \quad (32)$$

---

* *Proc. Roy. Soc., A*, **117, 549 (1928).**

† *Phil. Mag.*, **28, 633 (1914).**

‡ *Phys. Rev.*, **21, 623 (1923).**

§ *Loc. cit.*

|| *Loc. cit.*

where r is the fraction of the electrons reflected at the boundary from those incident on the metal from the gas phase; r may depend on the temperature.

Now the numerical value of $2\pi mek^2/h^3$, when the current is reckoned in ampères per square centimetre, is approximately 60, and it has been found that the best determinations of the electronic emission for the metals tungsten, molybdenum, tantalum and platinum, in a very pure state, agree very well with this value, that is, with making $g(1-r)=1$. The emission observed, however, from metals affected by surface impurities, *e.g.*, thoriated—tungsten filaments and oxide-coated filaments used in Wehnelt cathodes, do not agree with this value, but require smaller values, as small sometimes as 3 ampères per square centimetre. According to the classical theory the reflection coefficient r is practically zero, whereas direct experiments never suggested a zero reflection, but rather a value of the order of $\frac{1}{2}$. The present theory is far more satisfactory in suggesting that taking, as we have done hitherto, g equal to 2, the minimum value of r is about $\frac{1}{2}$, and occurs for perfectly clean metallic surfaces. The maximum remains, as before, at 1, and the theory is then in full accord with direct experiment.

An interesting feature of equation (32) is that the coefficient $2\pi emk^2/h^3$ is independent of the nature of the metal, a principle originally derived by Richardson [*] from the laws of thermodynamics, whereas the exponential factor, like b_0 in the equation derived from classical thermodynamics, depends upon the nature of the emitting surface.

14. Photo-electricity. According to the quantum theory, the photo-electric effect results when a quantum of light energy is given to an electron originally at rest in a metal. The electron may then escape from the metal, after suffering a reduction in its kinetic energy of at least W_a at the boundary-surface of the metal. It may also lose energy on its way to the surface. According to classical statistics, the electron, if it belonged originally to an electron gas, would possess negligible energy compared with that given to it by the quantum, but according to the new statistics theory the electrons possess energy ranging up to W_i, so that if ν_0 is the frequency of the incident radiation, the electrons most easily removed will be ejected from the metal if,

---

[*] See Richardson, "Emission of Electricity from Hot Bodies," pp. 55, 170.

$$h\nu_0 = W_a - W_i = W_a - \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad (33)$$

In general, a quantum of radiation, frequency ν, strikes the metal and is absorbed by one of the free electrons, of energy ϵ. This is not a possible process for genuine free electrons, but there is nothing to prevent its happening in the metal. The electron then has energy $h\nu + \epsilon$, and can escape from the metal with energy ϵ' where,

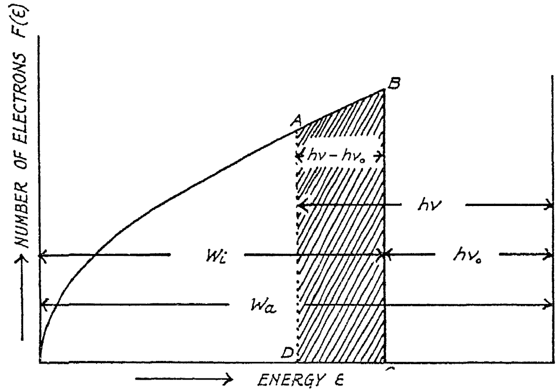


FIG. 10.—Photo-electric effect. (Fermi-Dirac statistics.)

$$\epsilon' \overset{=}{\underset{<}{\text{or}}} h\nu + \epsilon - W_a.$$

Since $\epsilon \overset{=}{\underset{<}{\text{or}}} W_i$, we have,

$$\epsilon' \overset{=}{\underset{<}{\text{or}}} h\nu - (W_a - W_i) = h\nu - h\nu_0.$$

In other words, there is a sharp *photo-electric threshold*, of frequency ν_0, and no electrons are emitted if the frequency of the incident radiation is below this value as given by equation (33). The sharpness of the limit comes from the almost complete absence of electrons, at these temperatures, with energy greater than W_i, together with the distribution law for the energies of the bound electrons.

The number with energies between ϵ and $\epsilon + d\epsilon$ is, from equation (10), proportional to $\epsilon^{\frac{1}{2}}d\epsilon$. If the electrons, of any energy, are approximately equally likely to absorb the quantum of ν-radiation, and we ignore energy changes subsequent to absorption, we get a spectrum of emitted electrons with the energy distribution, shown in Fig. 10. All electrons represented by the area ABCD can reach the required critical velocity on absorption of the radiation, hence the observed sharp photo-electric threshold at frequency ν_0, and the increase in emission as ν is increased beyond ν_0. In practice BC is not exactly a vertical straight line, but a rapidly falling exponential curve, since a more exact formula for the various numbers of electrons of energy ϵ, at temperature T, and therefore of photo-electrons of energy ϵ', on the foregoing assumptions is, equation (24),

$$n(\epsilon')d\epsilon' = \frac{4\pi}{h^3}(2m)^{\frac{3}{2}}\frac{\epsilon^{\frac{1}{2}}d\epsilon}{e^{(\epsilon - W_i)/kT} + 1},$$

where $\epsilon' = \epsilon + h\nu - W_a$.

Since W_i and $h\nu_0$ are of the order of 5 volts, W_i/kT is approximately 200 at room temperature. Thus, in the photo-electric current, electrons of energy greater than $h\nu - h\nu_0$ by 1 per cent. of $h\nu_0$ are infrequent, and greater by 3 per cent., 400 times less frequent than the commonest. Hence the frequency threshold is equally sharp.

Shifts of the photo-electric thresholds are produced by strong accelerating electric fields, and are of interest since they involve changes of the work function of a surface, without alterations of the other important characteristics of the metal. It is found that the form of the photo-electric sensitivity—frequency curve changes with the thresholds in intense fields. Thresholds are not sharp, but approach the frequency axis tangentially. Lawrence and Linford * used fields as high as 63,000 volts per centimetre, which shifted photo-electric thresholds towards the

* *Phys. Rev.*, **36**, 482 (1930).

red, the shifts being approximately proportional to the square roots of the applied fields. Their observations are in excellent agreement with the theory of the photo-electric effect, based on the Fermi-Dirac distribution of electrons in metals.

15. Electron Emission in Intense Electrical Fields. A very intense electrical field, applied near the surface of a metal, extracts electrons from the metal, even when it is cold. This phenomenon is often referred to as *a cold discharge.* The current varies very rapidly with the applied voltage, but under proper conditions it is reproducible and is a continuous function of the applied voltage over a wide range. At a given voltage the currents are independent of the temperature, but as the higher temperatures, at which ordinary thermionic emission begins, are approached, the strong field emission does become sensitive to temperature, and finally blends into the thermionic emission.*

An approximate theory of the effect was first developed by Schottky,† and recently the theory has been considered afresh by Richardson ‡ and by Houston.§ For low temperatures Millikan and Lauritsen || suggest the formula :

where I is the electronic current, X, the field strength, C, a constant and b, another constant the value of which can be obtained from thermionic data.

At higher temperatures the formula becomes :

$$I = A(T + c_1X)^2e^{-b/(T + c_1X)}, \quad . \quad . \quad . \quad . \quad (34)$$

where A and c_1 are constants.

Millikan and Lauritsen assert that a distinction should be drawn between the electrons which can function as thermions, and the ordinary conduction electrons which yield the emission at great field strengths and are absolutely independent of the temperature. Fowler and Nordheim ¶ query this statement. Using

---

* See Millikan and Eyring, *Phys. Rev.*, **27**, 51 (1926).

† *Zeits. f. Phys.*, **14**, 80 (1923).

‡ *Proc. Roy. Soc.*, *A*, **117**, 719 (1928).

§ *Zeits. f. Phys.*, **47**, 33 (1928).

|| *Proc. Nat. Acad. Sci.*, **14**, 45 (1928).

¶ *Proc. Roy. Soc.*, *A*, **119**, 173 (1928).

Sommerfeld's picture of a metal they fail to find any theoretical justification for equation (34). A single set of free electrons, distributed according to the Fermi-Dirac statistics, suffices for both purposes. They make the cold emission begin to be sensitive with fields of rather more than 10^7 volts per cm., so that the emission would be already very large for fields of the order 10^8 volts per cm. These values, higher than those commonly found in experiments, are taken to indicate measurable emission for values of X about 10^6 volts per cm. The absolute determination of X is, however, very difficult, owing to the large effect of minute surface irregularities, near which are found higher values of X than those derived from the geometry of the apparatus. There is also the possibility of sensitive spots on the surface, with a reduced value of the work function. An investigation by Rother [*] seems to support this view, for he finds that after very careful preliminary heat treatment, a value of X as large as 10^7 volts per cm. is required to extract a reasonable current.

Fowler and Nordheim derived the following formula, applicable at low temperatures :

where c_1 and c_2 are constants which can be calculated when W_i is known. More recently, this formula has been subjected to a rigorous experimental test in an extensive investigation by Stern, Gossling and Fowler.[†] Their results justify the application of Sommerfeld's theory to the phenomenon of electron emission in intense electric fields.

16. Thermo-electric Phenomena. Sommerfeld's expression for the Thomson coefficient is :

$$\frac{2\pi^2}{3}\,\frac{mk^2}{\mathbf{e}h^2}\left(\frac{2\pi g}{3n}\right)^{\frac{2}{3}} T.$$

Classical statistics gives a value of the coefficient which is much greater than that found experimentally, but the new statistics predicts a value which is only about 1 per cent. of that given by the classical theory at room temperature, assuming that the free electrons are equal in number to the atoms. Experiment als indicates that the Thomson coefficient is proportional to T, it should be according to the new statistics.

---

[*] *Ann. d. Phys.*, **81**, 316 (1926).

[†] *Proc. Roy. Soc., A*, **124**, 699 (1929).

The expression for the Peltier coefficient according to classic statistics is :

$$\frac{kT}{\mathrm{e}} \log \frac{n}{n_0},$$

whereas using the Fermi-Dirac statistics, Sommerfeld obtaine

$$\frac{2\pi^2}{3} \frac{m(kT)^2}{\mathrm{e}h^2} \qquad 3n \qquad 3n_{,}$$

where n and n_0 are the electron concentrations in the two metals. The numerical value, using the latter expression, is very considerably less than the intrinsic potential difference between the metals—a fraction of a millivolt. This is the order of magnitude of the Peltier coefficient as observed experimentally. Both theories give the same order of magnitude but, whereas according to classical statistics the intrinsic potential difference between two metals is generally small, according to the new statistics it is usually large and the Peltier coefficient is only a small fraction of it.

Stern * has pointed out that, in general, there exist two classes of phenomena associated with electricity in metals :

(*a*) Phenomena connected with the flow of electricity in closed circuits, which may be investigated only by making use of transport theories, and ;

(*b*) Phenomena associated with insulated conductors, which may be investigated by general theories of equilibrium.

With the new statistics serious discrepancies occur between the results obtained by the transport and equilibrium theories, and these discrepancies are due to the illegitimate application of theories of the latter type to essentially transport problems. It is only on the classical theory—or a theory which involves a linear dependence of the kinetic energy of the electrons upon the electron density—that these discrepancies vanish. Further, Stern shows that the equilibrium theory cannot always be used alone to consider problems of a transport nature in cases where the electron distribution obeys the Fermi-Dirac laws.

---

* *Proc. Roy. Soc.*, *A*, **126**, **570** **(1930)**.

In particular, he obtains two different values for the Thomson coefficient. In the first case it is assumed that the passage of electricity in a conductor consists of a gradual drift of the whole equilibrium distribution of electrons along a potential gradient. The value of the Thomson coefficient is then :

$$\left(\frac{\pi}{3n}\right)^{\frac{2}{3}},$$

In the second case he considers a small region about a point in a conductor where there is, before the motion, an excess of electrons, and assumes the conduction of electricity as consisting of the passage of this wave, so to speak, of excessive concentration to a region about a point at a higher temperature. Under these conditions the Thomson coefficient is :

and both the expressions differ from that obtained by Sommerfeld, who employed the transport theory.

Other phenomena dealt with by Sommerfeld include the Hall effect, and various allied thermomagnetic phenomena.

A defect in his work is the neglect of the interaction of electrons and atomic cores in calculating the statistical distribution. No theory of metals can be regarded as adequate which does not include the assembly of electrons and atomic cores in one system, to be treated as a whole. Lennard-Jones and Woods * attempted to find the average distribution of electrons in a metal, considering the atoms as long and chain-like, packed in a two-dimensional square array. Fowler † has dealt with the problem by calculating the average properties of an assembly, summing over all parts of the generalised phase-space. The ultimate results are the same as those obtained in the usual way.

---

* *Proc. Roy. Soc.*, *A*, **120**, 727 (1928).

† *Ibid.*, **113**, 432 (1926).

In addition, this method is capable of dealing with the theory electrolytes and assemblies of ions and electrons, as in giant star

BIBLIOGRAPHY

Brillouin. "Les Statistiques Quantique."
Darmois. "Statistique Mathématique."
Darrow. *Physical Review*, Supplement, 1, 90 (1929)
Fowler. "Statistical Mechanics."
Rice. "Introduction to Statistical Mechanics."
Tolman. "Statistical Mechanics."

CHAPTER III

THE GENERAL PROPERTIES OF MATTER

1. High Pressure Effects. The properties of matter under changes of condition, produced by hydrostatic pressure, are important, since, according to the new quantum mechanics, matter in bulk may have properties not deducible from the measurable properties of its smallest parts. But in order that hydrostatic pressure may produce significant changes, it must be of the same order of intensity as the atomic, or molecular, forces themselves, and these, for ordinary solids, or liquids, are of the order of tens of thousands of kilograms per square centimetre.

Many experimenters have investigated high pressure effects, and this branch of physics has been the subject of exhaustive investigation by Bridgman * over many years.

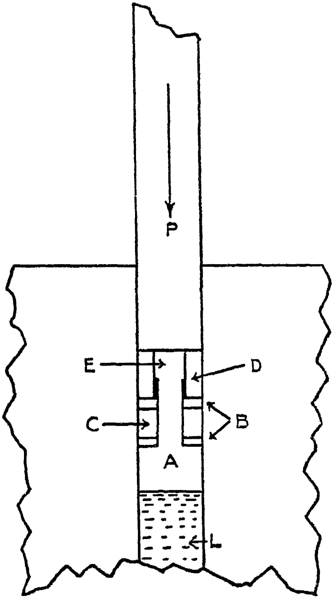


FIG. 11.– High pressure technique (Bridgman).

In the technique he used a packing of special design, which automatically becomes tighter at higher pressures, so that the only limit to the attainable pressure is set by the cohesive strength of the walls of the containing vessel. The manner in which th automatic tightening of the packing is produced is shown in Fig 11, which represents a section of a cylinder in which pressure i generated in a liquid, L, by the advance of a piston of hardene steel, P, driven by a hydraulic press. The mushroom-shape plug, A, carries a collar, C, of soft rubber packing. The plu with the packing is pushed forward by the piston, P, acting on th intermediary ring of hardened steel, D. The space, E, at the en of the stem of the mushroom is empty, so that the total pressur exerted by the ring of rubber must equal the total pressure exerte by the liquid on the head of A, and since the area of the ring i less than the area of the head, the pressure in the rubber i always greater than that in the liquid by the ratio of the area and the liquid can never leak. The packing is prevented fro escaping by rings, B, of mild steel, or copper. By the use of allo steels, and of vessels of small size, so that the beneficial effec of heat treatment may be extended throughout the entire wal pressures up to more than 20,000 kg. per sq. cm. can be handle and measured with an accuracy of 0·1 per cent. In most Bridgman's experiments, however, the pressures extended to onl 12,000 kg. per sq. cm. in the interests of the economical life the apparatus. Some of the more important results obtained a as follows.

---

* *Proc. Phys. Soc.*, **41**, 341 (1929) ; *Am. Acad. Sci., Proc.*, **66**, 185 (1931). See also Basset and Dupinay, *Comptes Rendus*, **191**, 1295 (1930) ; Hildebrand, *Phys. Rev.*, **34**, 649 (1929).

The change of volume of any truly homogeneous substanc free from internal strains, is entirely reversible with pressure ; permanent change of volume has ever been observed in suc materials up to pressures at least as high as 25,000 kg. per sq. c Contrary statements sometimes made are to be explained, eith by flaws in the material, or else by failure of the pressure to truly hydrostatic, such as when it is transmitted by an oil whi freezes under pressure, thus producing permanent changes of figu in the material.

In the case of gases there are effects at high pressure whi would not naturally be inferred from the behaviour at low pre sures. Fig. 12 shows one such effect, namely, the change volume in cubic centimetres per gram-molecule, starting from t volume at a pressure of 3,000 kg. per sq. cm. as the fiducial volum for the five gases, H_2, He, NH_3, N_2 and Ar. The significant feature is the crossing of the curves for N_2 and He; it is also evident that the curves for H_2 and Ar will also cross at a pressure slightly higher than that shown in the figure. This can be explained as follows. At comparatively low pressures, the decrease of volume of a gas has its origin in a decrease of the empty space between the atoms, or molecules, but as the molecules are urged into closer contact, this effect becomes exhausted, and at high pressures this contribution to compressibility disappears. But there is another factor in the compression, namely, the actual loss of volume of the molecules themselves, and this evidently may persist at pressures where the initial effect no longer exists. This dual mechanism is doubtless the explanation of the striking difference between He and N_2. The atom of He is much smaller

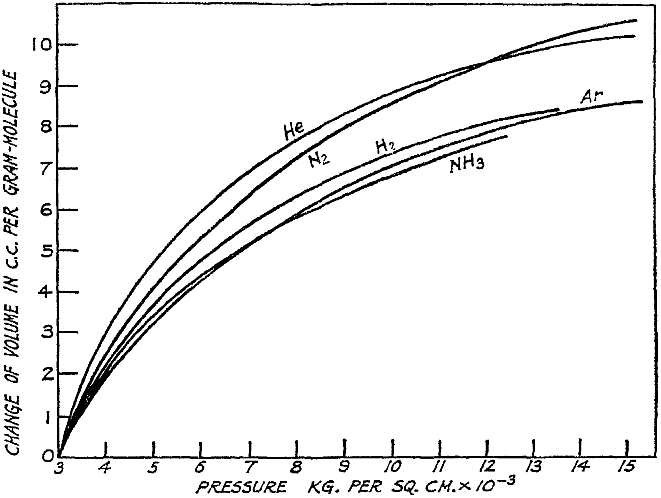


FIG. 12.—Change of volume as a function of the pressure. At 10,000 kg. per sq. cm. the order of the curves, reading from the top downwards, is helium at 55°, nitrogen at 68°, hydrogen at 65°, argon at 55°, ammonia at 30° C.

than the molecule of N_2, so that at low pressures the decrease of volume of He is greater than that of N_2. But at high pressures the decrease of volume of N_2 becomes greater than that of He, because the structure of the N_2 molecule is so much more complicated than that of the He atom, that it has in it the potentiality of much greater loss of volume. Similar considerations also explain the relative behaviour of H_2 and Ar. The molecule of H_2 is normally smaller than the atom of Ar, and so at low pressures the compressibility of H_2 is greater than that of Ar. But at high pressures the *rôles* are reversed, because the electronic structure of atomic Ar is so much more complicated than that of molecular H_2, that the atom of Ar is capable of much greater loss of volume than the molecule of H_2.

This behaviour is typical of all substances at high pressures. Beyond the first few thousand kilograms per sq. cm., the major part of the loss of volume is provided by the atoms, or molecules themselves, and those substances with the most complicated, or the most loosely constructed molecules, have the greatest compressibility at high pressures, although at low pressures the behaviour may be the reverse.

The most striking fact in the compressibility of liquids is that the volume changes of many liquids tend to approach much more nearly to equality at high pressures than at low ones. Measurements on fourteen common liquids, including the first five alcohols ether, CS_2, C_2H_5Cl and water, show an extreme variation in the loss of volume under a pressure of 12,000 kg. per sq. cm., from 21 per cent. for water, the least compressible, to 33 per cent. for ether, the most compressible, which thus loses only 50 per cent more volume than water, although its initial compressibility is four or five times greater.

The compressibility of liquids drops very rapidly with increasing pressure. At 12,000 kg. per sq. cm. the compressibility o common organic liquids varies from 1/14*th* to 1/20*th* part of the initial compressibility; half of this decrease in compressibility i accomplished in the first 1,000 kg. per sq. cm., and at 6,000 kg per sq. cm. 95 per cent. is completed. Qualitatively, there i thus much similarity between liquids and gases. As in the cas of gases, the initial high compressibility of liquids arises from the elimination of space between the molecules, whereas the part of the compressibility which persists at high pressures probably arises from the decrease of volume of the molecules themselves. Liquid metals have a lower order of compressibility than organic liquids. Glycerine, which has a fairly complicated molecule, is only two-thirds as compressible as water at 12,000 kg. per sq. cm.

Thermal expansion decreases with increasing pressure, but the decrease is much less than that of compressibility ; the thermal expansion under 12,000 kg. per sq. cm. is, on the average, between one-fourth and one-fifth of its initial value, compared with a four fold decrease in compressibility. Also, the thermal expansions of fourteen liquids, with the exception of water, approach much more closely to equality under 12,000 kg. per sq. cm. than do the compressibilities, the extreme variation being only 25 per cent., from $2{\cdot}4$ to $3{\cdot}0 \times 10^{-4}$. As the temperature approaches the absolute zero, the compressibility falls only slightly, while the thermal expansion decreases to zero, but at high pressures the compressibility drops much more than the thermal expansion.

At atmospheric pressure the thermal expansion of all liquids increases with rising temperature, but in the neighbourhood of 3,000 kg. per sq. cm. there is a reversal, and at still higher pressures the thermal expansion is greater at lower than at higher temperatures. The explanation is probably connected with the known fact that if the molecular restoring forces are linear functions of the molecular displacement, thermal expansion vanishes, so that a high thermal expansion means high departure from linearity. The smaller the volume of a substance, the greater, in general, the departure of the forces from linearity, since the repulsive forces which predominate at small volumes vary inversely as some high power of the distance. At constant pressure the volume is less at low temperature, and so the departure from linearity would be expected to be greater, thus accounting for the greater thermal expansion. At low pressures there is a reversal of this behaviour, because there is another mechanism active, the properties of the liquid tending to approach more nearly to those of a gas, *e.g.*, high thermal expansion, particularly at higher temperatures.

The volume behaviour of solids is qualitatively different from that of liquids, or gases. The compressibility is generally less, as is to be expected. There seems to be no exception to the general rule that the compressibility of a substance in the solid phase is less than that of its own melt. This is true for normal substances which contract on freezing, and also for water and bismuth, which expand on freezing. It is thus evident that the lattice structure of itself imparts a certain stiffness foreign to the liquid. Also the initial domain of high compressibility, followed by very much lower compressibility, which is characteristic of liquids, is much less prominent in solids, the compressibility of which decreases comparatively little at high pressures. It is therefore probable that by far the greater part of the compression of a solid has its origin in the compression of its atoms.

As a general rule, the compressibility of solids decreases at high pressures by amounts which increase with the compressibility, as might be expected, but there are exceptions. The compressibility of pure quartz glass, SiO_2, and a number of compound glasses in which the content of SiO_2 is high, increases with increasing pressure by an amount far beyond experimental error. The compressibility of K drops off with increasing pressure much less than that of Rb or Cs, so that although initially the compressibility of Cs, for example, is nearly twice as great as that of K, at 12,000 kg. per sq. cm. it has become considerably less. The persistence of the compressibility of K is attributed to the abnormally loose structure of the atom of K, as shown by the abnormally high value of its atomic volume.

In the case of crystals it is found that only in those of the cubic type is the change of volume under hydrostatic pressure the same in every direction, so that to determine completely the effect of pressure on the volume of single crystals the linear compressibility must be measured in several directions. Bridgman found that this compressibility may vary much more with direction than might be expected from the difference of atomic spacing in different directions. Thus, the linear compressibility of zinc parallel to the hexagonal axis, is seven times as great as that at right angles, whereas the ratio of the atomic spacing in the two directions is only 7 per cent. different from that for spherical atoms in normal hexagonal piling, and, in fact, the spacing is compressed along the axis, while the compressibility is greater along the axis. The behaviour of tellurium is highly unusual, in that there is negative compressibility along the trigonal axis, *i.e.*, when exposed to hydrostatic pressure, a crystal of tellurium expands in the direction of this axis.

The compressibility of most of the alkali halides has been measured by Slater,* up to pressures so high that accurate values could be found for the change of compressibility with pressure. Although several theories have been proposed which give fairly good values for the initial compressibility, they all predict changes of compressibility with pressure which do not agree with experimental results.

Another interesting phenomenon is the change of state produced by high pressure. Now among the various ideas as to the ultimate relation between liquid and solid at high pressures which have been held at different times was one that there is a critical point between liquid and solid. Another theory postulated a maximum melting-point temperature, above which a substance was capable of existence only in the liquid phase, no matter how high the pressure. Bridgman's results, however, seem to disprove both these points of view, for measurements on nearly forty substances up to 12,000 kg. per sq. cm. and on water up to 21,000 kg. per sq. cm. show that if either of these two possibilities ever occurs, there must be a complete reversal of the universal trends in the experimental range of pressure. All melting-point curves, whether rising, *i.e.*, the melting-point temperature increases with pressure, or falling like those of water and bismuth, are concave toward the pressure axis. Furthermore, the difference of volume between liquid and solid, plotted against melting pressure, gives a curve convex towards the pressure axis, and the slope, dt/dp, of the melting-point curve, plotted against temperature, a curve convex towards the temperature axis. These facts indicate that there can be neither critical point nor maximum. Experiments also show that the melting-point temperature may not be raised indefinitely by the application of sufficiently great pressure, but the rate at which this temperature is elevated by a definite increment of pressure becomes continually less as the pressure increases.

---

* *Am. Acad. Proc.*, **61**, 135 (1926).

Bridgman also measured the difference of compressibility between different polymorphic forms of the same substance. In the majority of cases that one of two phases which has the larger volume, and which therefore is stable at the lower pressure, is the less compressible. It is also true, in general, that the phase of larger volume has the higher crystalline symmetry. It appears as if the molecules, or atoms, have some internal structure analogous in some respects to a framework of high symmetry and rigidity, such that at low pressures, where the intensity of the external forces is low enough to permit the natural arrangement, the molecules assume a disposition of high symmetry and low compressibility, with the projecting parts of the framework of different atoms in register with each other; but at high pressures the natural forces are overcome, the frameworks are pushed out of register, and the system collapses to an arrangement of smaller volume, of lower symmetry, and, because the frameworks are the most rigid part of the molecule, of greater compressibility.

Pressure affects the viscosity of liquids. In all cases, except the abnormal one of water, and then only over a limited range of pressure and temperature, viscosity increases under pressure, and by amounts varying enormously from substance to substance. The factor of variation under 12,000 kg. per sq. cm. is 1·33 for mercury, and 10^7 for eugenol. In fact, the pressure effect on viscosity, and its variation from substance to substance, is much greater than any other known pressure effect. Viscosity increases geometrically with pressure, that is, the logarithm of viscosity is approximately a linear function of the pressure. There is a very close correlation between the magnitude of the pressure effect and the complexity of the molecular structure, the pressure coefficient being least for monatomic mercury and greatest for complicated substances like eugenol. It is evident that no purely kinetic mechanism of viscosity, such as we have in gases, is competent to explain such enormously large effects. There would seem to be little question that a large part of the viscosity of a liquid is purely mechanical in origin, arising from an interlocking of the molecules. Such a mechanism is consistent with the very large pressure effects, and the enormous variations of the effect with molecular complexity.

Recently, Bridgman measured the effect of pressure on the shearing modulus of several isotropic substances.* The rigidity of Fe increases under pressure, as would be expected, the increase being about 2·5 per cent. for 12,000 kg. per sq. cm. The rigidity of glass, on the other hand, decreases by amounts varying with the composition from 0·7 per cent. to 11 per cent. for 12,000 kg. per sq. cm. The effect is largest for those glasses which have the abnormal increase of compressibility with pressure, as might be expected. By combining this change in the shearing modulus with the known changes in density, it may be calculated that the velocity of a wave of shear decreases under a pressure of 12,000 kg. per sq. cm. by amounts varying from 2 to 6 per cent. Similarly from the pressure coefficient of rigidity and the pressure coefficient of compressibility, the effect of pressure on Young's modulus may be found; this may increase, or decrease, under pressure, depending on the composition of the glass, by amounts varying from +2·5 per cent. to −10 per cent. at 12,000 kg. per sq. cm.

2. The Effect of Pressure on Thermal Conduction. Bridgman has measured the effect of pressure up to 12,000 kg. per sq. cm. on the thermal conductivity of eleven metals. Of these eleven metals, the thermal conductivity of five increases under pressure and that of six decreases. In only two cases does the Wiedmann-Franz ratio increase under pressure, and in the remaining nine it decreases by amounts varying up to 15 per cent. for Ni at 12,000 kg. per sq. cm. Since the Wiedmann-Franz ratio varies with pressure, it is obvious that the connection between electrical and thermal conductivity cannot be the universal and simple one of the original theory. A consideration of the contribution to the thermal conductivity by the atoms, as distinguished from the electrons, seems to offer a possibility of explaining at least part of the discrepancy, and would suggest that the contribution made by the atoms may be larger than is often supposed.

---

* *Am. Acad. Proc.*, **64**, **39** **(1929)**.

The effect of pressure on many liquids has also been measured up to 12,000 kg. per sq. cm. The thermal conductivity is increased by fairly large amounts, the factor of increase varying from 1·50 for water, the least compressible of the substances measured, to 2·74 for normal pentane, approximately the most compressible. It is very suggestive that this increase runs approximately parallel with the increase in the velocity of sound under pressure, as calculated from the change of density and the compressibility. Bridgman found a simple relation for the thermal conductivity of liquids, *viz.*,

$$k = 2\alpha v \delta^{-2},$$

where k is the thermal conductivity in absolute units, α, the molecular gas constant $2{\cdot}02 \times 10^{-16}$, v, the velocity of sound, and δ, the mean distance of separation of the molecules in the liquid, assuming them piled in simple cubic array. The formula represents, with considerable success, the thermal conductivity of normal liquids, of water, which is abnormal in so many respects, and also of non-crystalline solids, such as glass or hard rubber.

In gases the phenomena of viscosity are closely connected with those of thermal conductivity, but in liquids the difference in behaviour of the temperature coefficients of thermal conductivity and viscosity makes it highly probable that the mechanisms of the two effects are different.

3. The Effect of Pressure on Electrical Properties. Bridgman* has also investigated the effect of pressure on the electrical resistance of substances. Of forty-eight pure metals which he has measured, the resistance of thirty-nine decreases under hydrostatic pressures by amounts varying with the character of the metal, from 1 per cent. under 12,000 kg. per sq. cm. for Co to 73 per cent. for K. The relation between change of resistance and pressure is not linear, but the curve of resistance against pressure is always convex towards the pressure axis, which means that the effect of a given

* *Am. Acad. Proc.*, **64, 75**

increment of pressure becomes less at high pressures. In the case of K the initial rate of change is so great that the resistance would entirely vanish at a pressure of 5,600 kg. per sq. cm., if it continued at the initial linear rate. Six or seven of the forty-eight metals, Li, Ca, Sr, Sb, Bi, the low-pressure modification of Ce, and perhaps Ti, increase in resistance under pressure, and in all these cases the curve of resistance against pressure is convex toward the pressure axis, just as in the case of the metals with negative coefficient. But now the significance of convexity is that the effect of a given increment of pressure becomes greater at high pressures, which is not to be expected. The curvature for these two types is such that the curve for one could be regarded as a prolongation of that for the other, so we might anticipate that the resistance of all metals increases at sufficiently high pressures, the initial difference between various metals being ascribable to different internal pressures. Such an expectation is much strengthened by the discovery of three metals whose resistance does actually pass through a minimum with increasing pressure. The first of these is Cs, which is the most compressible metal, and therefore might be expected to show the effect most easily. The resistance of this at room temperature passes through a minimum of about 0·71 of the initial value between 4,000 and 5,000 kg. per sq. cm. The next is Ba, which stands to the right of Cs in the periodic table, and which has a minimum at 0·97 of the initial resistance at about 8,000 kg. per sq. cm. Rb also has a minimum at 18,000 kg. per sq. cm. of 31 per cent. of its initial resistance. Measurements on K show no minimum up to 19,000 kg. per sq. c.m., but results suggest one in the neighbourhood of 24,000 kg. per sq. cm. of 18 per cent. of its initial resistance. Similarly with Na there is probably a minimum at pressures considerably higher than 24,000 kg. per sq. cm. The resistance of Li increases continually with rise of pressure.

The irregularities of elements in the second column of the periodic table are more striking than the regularities. The resistance of Be decreases under pressure, whereas that of Li increases, Mg decreases, as does also Na, but Ca increases compared with the decrease of K, Sr increases against the decrease of Rb, and its increase is greater than that of any other metal, while, finally, Ba and Cs show minima, but the whole scale of the pressure effects on Ba is very much smaller than on either Cs or Sr.*

The effects of pressure on resistance are complicated, much more so than the effects of temperature, for example. A consideration of the pressure effects seems to imply that the electron mechanism must be much more complicated than the pure temperature effects would lead us to expect. Particularly, the occurrence of a minimum resistance is suggestive ; a minimum property nearly always involves the action of at least two mechanisms, which, to a certain extent, oppose each other.

When we pass on to consider binary alloys of metals, examples of a positive pressure coefficient of resistance are frequent, and in all cases the initial effect of adding a small amount of foreign metal to a pure one is to increase algebraically the pressure coefficient. That is, if the coefficient is initially negative, as it is in the majority of cases, adding a foreign metal makes the coefficient smaller numerically, while if the coefficient is initially positive, it becomes still more positive on the addition of another metal. This result is capable of a simple geometrical interpretation, consistent with the wave mechanics picture of electrical resistance as arising *from the scattering of electron waves by irregularities in the atomic* structure. For, in addition to the irregularities in the lattice structure of a pure metal, due to temperature agitation, there must be, in general, irregularity of a purely geometrical character when a foreign metal is introduced, arising from the unequal sizes of the two sets of atoms. The geometrical differences between the two sets are accentuated as they are urged into closer contact by pressure, so that the scattering of the electron waves, arising from this effect, increases, and the pressure coefficient becomes more strongly positive.

Thermal electromotive force is another electrical property that can be measured under pressure without great difficulty. The effects are considerable, for the thermal electromotive force of a couple composed of a metal in the uncompressed state, and the same metal compressed, approaches the order of magnitude of the thermal electromotive force of couples composed of ordinary dissimilar metals. For example, the thermal electromotive force of a couple composed of Zn uncompressed and compressed to pressures of 12,000 kg. per sq. cm., with its two junctions at 0° C. and 100° C., is one-third as great as that of a couple of uncompressed Zn and Pb between the same temperature limits.

---

* For other metals see Fischer, *Zeits. phys. Chem.*, **8**, 207 (1930).

The effects of pressure on thermal electromotive force may be exceedingly complicated, and vary greatly from one metal to another. In general, the effect of pressure on the Peltier and Thomson effects is positive, that is, the positive current absorbs heat in flowing from uncompressed to compressed metal, and the Thomson heat absorbed in passing from a low to a high temperature is greater in the compressed than in the uncompressed metal, but the irregularities are much greater than the irregularities in the resistance effects, and occur in unexpected places, the irregularity of thermal electromotive force being greatest for Sn, Fe, and Al, metals which under pressure are without special distinction in other respects. Just as in the case of resistance phenomena, these complex effects indicate a complicated mechanism, certainly more complicated than that contemplated in any theory yet proposed. There is as yet no discoverable parallelism between the effects of pressure on resistance and on thermal electromotive force, from which one may perhaps draw the conclusion that essentially different aspects of the electron mechanism are responsible for thermo-electric phenomena, and those of resistance.

4. High-Vacuum Technique. The importance of high vacuum technique needs no stressing, and during recent years rapid strides have been made in this direction, particularly in the methods of producing low pressures by means of high vacuum pumps, actuated by a vapour stream.

The first pump of this type was invented by Gaede,* who caused a stream of mercury to pass by a porous diaphragm connected with the vessel to be evacuated. Diffusion occurred in either direction. The gas diffusing into the mercury vapour was swept into a condensing vessel, and thence to a mechanical pump ; the mercury passing the other way was condensed in a special trap, and returned to the boiler. The diffusion was so slow that Gaede replaced the diaphragm by a slit 1 mm. wide. When the mercury vapour was maintained at a pressure yielding a mean free path of about 1 mm., the pump would exhaust at its maximum efficiency. The speed was limited by the size of the slit, but with wider slits the outcoming vapour prevented ingress of the gas, and the pump became inoperative. Langmuir [*] showed that if the mercury vapour could be given a sufficiently large forward velocity past the jet, the molecules would have little tendency to stray through the aperture, even at relatively high pressures.

---

* British Patent, 19,793 (1914).

To prevent molecules which had hit the wall from rebounding in the opposite direction, he cooled all the walls in the neighbourhood of the aperture, and thus permanently condensed the incident molecules. Langmuir's first pump had as essential parts a jet through which mercury vapour issued, a wide intake space corresponding with Gaede's slit, and a pumping region with cooled walls of a shape likely to conform with the natural spread of the mercury-vapour stream.

Although such a pump may be described as a preferred form, it is evident that a much simpler construction will achieve somewhat similar results. Thus a simple T-tube, cooled in water, has been patented by Buckley.[†] Vapour generated at the bottom of a long tube, in passing by a side tube, sweeps any gas naturally diffusing in towards the backing pump. Buckley[‡] further found that cooling at the aperture could be omitted, if the mercury vapour stream were cooled just below the jet to remove all molecules having an appreciable lateral component.

In all the foregoing pumps the condensed mercury must return by the same path as the vapour, and in opposition to its flow. This is disadvantageous because the mercury does not wet glass, but collects into globules, between the interstices of which gas may return in the contrary direction. The globules may also fall against the heated parts of the tube and generate vapour at unwanted points. Langmuir [§] obviated these drawbacks by an inverted construction, the condensed mercury travelling away from the jet.

---

[*] *Journ. Frank. Inst.*, **182**, 719 (1916).
[†] U.S. Patent, 1,433,258 (1922).
[‡] U.S. Patent, 1,371,734 (1921).
[§] U.S. Patent, 1,320,874 (1919).

Many other forms of pumps have been described *, from which we select the all-metal pump of Gaede.† This unit contains a number of condensation pumps in series, fed from a common source of mercury vapour. The latter is used to produce three different stages of vacuum, the first by diffusion, the third by jet ejector action, and the second by diffusion when the pressure is low and by ejector action when it is higher.‡

A tube 14, Fig. 13, connecting the upper and lower parts of the tube 18, joins the latter at 6 by means of a passage at the flange, and at this point it is provided with a tube for connection to the backing pump. Mercury vapour, developed in the vapour chamber inside tube 20, flows upwards through a conduit 21, and issues through the nozzles 19, 22 and 28. Any vapour which condenses in tube 20, collects and is returned to the boiler by way of the space between the concentric tubes 20 and 21, so that the vapour passing upwards through 21 is free from drops of mercury. It issues through the funnel-shaped annular

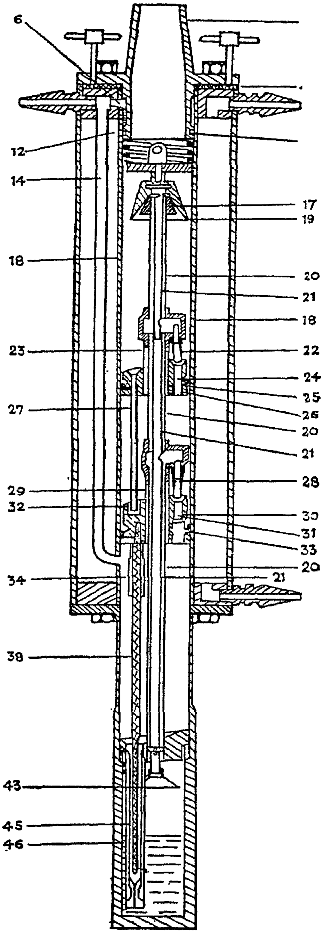


FIG. 13.—Gaede's all-metal mercury vapour pump.

---

* See Dushman, *Journ. Frank. Inst.*, 211, 689 (1931).

† *Zeits. f. tech. Phys.*, 4, 10, 337 (1923).

‡ Gaede 4-stage pumps are now in use.

space formed by the conical surfaces 17 and 19, and condensed mercury collects in, and fills, the space between the iron block 25 and the casing wall 18, above the leather packing 26, whence it drains off through the tube 27 into the cup 32. The space above 25 is hermetically sealed against the space below it by the tube 23, and by the mercury collected above the leather packing and the cup 32.

The arrangement at the lowest aperture of the tube 21 is a duplicate of that just described, the boring 31 being placed immediately in front, and in continuation, of the vapour passage, formed by the nozzle 28. Mercury, collecting above the leather packing 33 in the cup 34 and in the tube 29, closes the space above the iron cylinder 30 against the volume below it.

A steel rod 38, attached to the cylinder 30, extends down into tube 45, and tends to keep the mercury in 45 cool. The distance between tube 45 and the jacket 46, at the top where mercury flows into 45, is so small that no mercury can penetrate into the space between these tubes. This air jacket, together with the steel rod, counteracts the heat of the vapour from the boiler, and prevents mercury in tube 45, which reaches to the line 43, from being heated to the boiling point and thereby being expelled from the tube.

Nozzle 1 connects the vessel being exhausted to the pump, and the high vacuum side is sealed against the backing pump by the mercury column in the annular space 4, formed by the tube 9 and the wall of the casing 18 above the constriction 12.

The first and second sections function as auxiliary pumps to the third, and uppermost, section, the latter acting as a high vacuum pump of very great efficiency. In this third section the vapour jet issues with a high velocity from a ring-shaped nozzle 19, and is directed downwards along the cooled wall of the pump. The vapour pressure at this nozzle is so small that the mean free path of the molecules is of the same magnitude as the distance between the wall of the casing 18 and the nozzle 19.

In the lowest section vapour, issuing from a conical nozzle 28, adapted to accelerate its velocity, reaches its highest velocity and minimum pressure. Within the mixing nozzle 31 the pressure in the jet again increases, attaining a value equal to that in the backing pump, and at the same time the velocity is diminished. The minimum pressure reached at the point where the vapour jet enters the " mixing " nozzle is 1 mm., and the mean free path of the molecules is small compared with the width of the slit, which is 2 or 3 mm. This arrangement, therefore, cannot operate on the diffusion principle, and the motion of the gas issuing from the vessel to be exhausted is not decided by the difference in the partial pressures of the gas, but by the difference in the total pressure of gas and vapour. Consequently the pressure does not fall below 1 mm., but as long as its value is above 1 mm., gas will pass towards the point of lowest pressure at the slit, will mix with the jet vapour, and, after compression in the " mixing nozzle," will be carried away to the backing pump. The second section also operates on the jet principle, providing the vapour pressure in the slit between the accelerating nozzle 22 and the " mixing nozzle " 24 is so great, that the mean free path of the molecules is small compared with the slit's width. When the pressure between the two lower sections, *i.e.*, between the iron blocks 25 and 30, falls to 5 mm., or less, the minimum pressure at the slit becomes so small that the molecular free path is of the same order of magnitude as the width of the slit, and gas from the vessel being exhausted penetrates the jet by diffusion. The exhausting action of the pump does not cease, therefore, when the gas pressure equals the minimum vapour pressure at the nozzle, but continues to decrease as the gas follows the partial pressure gradient. The width of the slit has been adapted for this double action, and all three sections co-operate to give the highest possible efficiency at various pressures.

Gaede * has recently designed a diffusion pump which has an exhaust capacity fully eight times that of the 3-stage pump. The essentially new part is a double cooling arrangement. This is necessary in order that the mean free path of the gas molecules, to be entrained in the stream of mercury vapour, becomes large enough in comparison with the large dimensions of the diffusion pump.

There remains as an inherent drawback to the mercury diffusion pump the necessity for a cooled trap to prevent any mercury vapour from diffusing into the evacuated vessel. This difficulty can be overcome by using certain other metals in the place of mercury. Housekeeper [*] has explored the possibilities of the lower melting-point metals such as zinc, cadmium, tin, lead and bismuth. The first two will vaporise and condense at temperatures appreciably below their melting points, and it is not easy to return the condensed metal to the boiler. He has designed a reversible pump in which condenser and boiler are symmetrically placed with regard to the pumping aperture, and the metal can be driven alternatively from one side to the other. A simpler vertical pump uses lead, tin, or bismuth which melt before they vaporise. It is interesting to note that although the condensing portions must be kept relatively cool, in actual practice the walls have to be heated externally to prevent solidification. Both Housekeeper [†] and Snook [‡] have described large industrial pumps, constructed of metal, employing in the first case an electric arc, and in the second a carbon resistance furnace to vaporise the metal.

---

* See Gaede and Keesom, *Comm. Phys. Lab. Leiden,* No. 195.

Recently, Burch [§] has discovered that certain high-boiling fractions, separated during the vacuum sublimation of petroleum residues, may be used in condensation pumps. The oils have vapour pressures probably less than 10^{-6} mm. of mercury at room temperature, and are thus usable without the customary liquid air trap. These liquids represent a very real advance in vacuum technique, because they can replace mercury without special precautions, or complication of the apparatus. They have, however, certain peculiarities of their own.

When petroleum jelly is distilled in the evaporation still, the residue at 320° C., amounting to about 13 per cent. of the original jelly, is a substance not unlike common vacuum grease. The saturation vapour pressure of this substance is rather less than 1 microbar [||] at 320° C. Experiments on the vapour pressure of this substance, involving evaporation, the condensing surface being cooled by liquid air, showed that the vapour pressure was less than 10^{-3} microbar at 70° C. With the aid of this grease, then, ground joints can be freely employed in highly evacuated systems.

---

[*] U.S. Patent, 1,471,661 (1923).

[†] U.S. Patent, 1,461,190 (1923).

[‡] U.S. Patent, 1,471,012 (1923).

[§] *Proc. Roy. Soc., A*, 123, 271 (1929).

[||] A bar is a pressure of 10^6 dyne per sq. cm.

Using the residue obtained at 118° C. in a single stage metal condensation pump, designed for a fore-vacuum of 10–20 microbars, the pressure in a vessel was reduced to less than 2×10^{-3} dyne per sq. cm., as measured with an ionisation gauge. The degree of vacuum obtained appeared to be limited by gas evolution from the electrodes and bulb of the gauge. At 1 dyne per sq. cm. the speed of the pump was rather greater than 2,000 c.c. per sec. At higher pressures it was limited by the speed of the backing pumps. It was possible to exhaust a discharge-tube, fitted with a metal window, to a degree sufficient for the application of 300 kilovolts. Burch attempted to measure the ultimate pressure attainable with such a pump by means of an ionisation gauge. The whole of the glasswork was heated to drive off occluded gases, which otherwise would make their appearance during exhaustion. No ionisation current could be detected with the instruments available, although an ionisation current, corresponding to 10^{-4} dyne per sq. cm., could have been detected.

Hickman and Sanford * have also investigated the use of organic liquids instead of mercury in condensation pumps, and, in addition, they have experimented with various designs of pumps. Every pump tested worked at least as well with mercury as with an organic liquid. The most suitable liquids are equal to, or better than, mercury in speed of exhaustion, but they require a lower backing pressure. Of some twenty high-boiling organic liquids examined, only the higher hydrocarbons and the esters of phthalic acid proved useful. The hydrocarbons were less efficient because :

(*a*) They showed inferior pumping speed.
(*b*) They decomposed slightly.
(*c*) They charred with continual use.

The phthalates were found convenient on account of good pumping speed, stability, the ease with which they could be obtained pure, and their low vapour pressures. Of the phthalates, butyl benzyl phthalate is the most efficient member of high boiling point, but is not easily obtainable. Failing this, n-di-butyl phthalate is recommended for use in pumps as a satisfactory substitute for mercury. For many purposes it does not require a condensing trap, and on other occasions a bath of ice and salt, or solid carbon dioxide in acetone, provides sufficient cooling.

---

* *Rev. Sci. Inst.*, **1**, 140 (1930).

The miniature glass pump is recommended, because it is generally large enough for laboratory vacuum requirements, and the cooling is easily accomplished.

For the measurement of very low pressures there are many manometers available, ranging from the McLeod gauge to the Knudsen manometer. The ionisation gauge is now widely used to measure the lowest pressures.

If a gas is present in a 3-electrode thermionic valve in quantity not sufficient seriously to affect the filament activity, and the plate voltage exceeds a value necessary to produce ionisation of the gas in the valve, it has been found that the number of ions produced is proportional both to the gas pressure and to the electron current passing through the gas. If a small negative potential is now applied to the grid, a certain fraction of the positive ions will be drawn to it, and their number can be accurately determined from the current flowing in the grid circuit. The equation for such a gauge may be written in the form :

$$p = \frac{kI}{i},$$

where p is the gas pressure, I, the positive ionisation current, i, the electron current and k, a constant of the gauge.

As the value of i must be known, and as the emission from the filament is liable to vary somewhat with the kind of gas and with its pressure, it is advantageous, if many readings are to be made, to place in the circuit measuring i the coils of a relay, which is adjusted to close at a definite value of i, and which, when closed, cuts in a shunt across the filament. This shunt reduces the heating current.

King * found that the pressure in such a gauge is proportional

---

* *Journ. Opt. Soc. Amer.*, **8**, **145** (**1924**).

to the ionisation current at pressures as high as $1{\cdot}5 \times 10^{-3}$ mm., if the electron current is 20 milliamp. and the voltages on the plate and grid are + 110 and —2 volts, respectively, but the lower limit is determined largely by the sensitiveness of the current reading instruments.

Found and Dushman,* using gases and vapours, confirmed the formula :

$$p = kI.$$

Measurements of the vapour pressure of vacuum oils at different temperatures have been made, the values ranging from $7{\cdot}5 \times 10^{-6}$ mm. to $7{\cdot}5 \times 10^{-5}$ mm. at 0° C., and from $1{\cdot}5 \times 10^{-4}$ to $1{\cdot}5 \times 10^{-3}$ mm. at 25° C. The vapour pressure of ice at temperatures between —50° C. and —78° C. was also measured.

An approximate value of a gas pressure may be calculated as follows, *e.g.*, Burch, † using a particular low-power transmitting valve with 1,770 plate voltage, and —20 volts on the grid, found the anode current to be 23·7 milliamps, and the grid current less than —0·2 microamp. Now the ratio—reverse grid current to anode current—gives the expectation of ion production by an electron moving from filament to anode. This expectation is proportional to the gas pressure, and is dependent on the velocity of the electron. The expectation for electrons of various velocities passing through 1 cm. of air at atmospheric pressure is about 7,700 at 1,770 volts. When the varying speed of the electrons, as they pass from filament to anode, is taken into account, it is found that the actual expectation of ions is about 0·465 times the expectation if the electrons all had the most favourable velocity across the whole of the inter-electrode space. The ratio—grid current to anode current—was 1/118,000, and the distance traversed by the electrons, *i.e.*, grid-anode distance, 1·2 cm., so that the expectation of ion production was less than 1/118,000, and 0·465 × 7,700 ions were anticipated per centimetre-atmosphere. The pressure was accordingly :

$$\frac{1}{[71{\cdot}2] \times 0{\cdot}465 \times 7{,}700 \times [>118{,}000]} \text{ atmosphere,}$$

or

$$< 2 \times 10^{-3} \text{ dyne per sq. cm.}$$

---

* *Phys. Rev.*, **17,** 7 (1921).

† *Proc. Roy. Soc., A,* **123,** 283 (1929).

It is evident, therefore, that the ionisation gauge may be used to measure the lowest attainable pressures.

Molthan * has recently described a new type of ionisation gauge. A tube, attached to the evacuated system, contains four conducting elements, of which one is a filament emitting electrons, two are field regulators, and the fourth is an electrode, the positive charge of which (derived from the space charge) is a measure of the space charge and, therefore, of the gas pressure. The fourth electrode is connected to the anodes of two valves in parallel, the filament currents and the grid potentials of which are so adjusted that the system has a linear potential-current characteristic for a potential range, 0·5–5·0 volts. The anodes in turn are connected to a single-fibre electrometer. Calibration curves show a linear relation between ionisation current and pressure of the gas, the lower limit of measurement being in the region 10^{-10} mm. of mercury.

5. The Flow of Gas at very Low Pressures through a Hole in a Thin Plate. It is sometimes required to calculate the amount of gas flowing through a hole in a thin plate, when the diameter of the hole is small compared with the mean free path of the molecules. If p_1 and p_2 are the pressures on the two sides of the plate, the resultant mass of gas which passes through one square centimetre per second is given by † :

$$(p_1 - p_2)\sqrt{M}$$

where M is the molecular weight of the gas, R, the gas constant per gram-molecule and T, the absolute temperature. The vapour pressure of highly refractory metals may be determined with the help of this formula. Egerton ‡ has measured the vapour pressures of zinc, cadmium and lead, the metals being contained in a small pot provided with a hole of known area. After weighing the pot, it was placed in a silica tube within which a high vacuum was maintained ($p_2 = 0$), and the tube was inserted in a hole in a large block of copper, maintained at a constant temperature. The pot was again weighed at the completion of the experiment, and the loss in weight gave the amount of vapour that had escaped from the orifice. Thus p_1 could be determined. A correction must be applied for the number of molecules that return from the far side, through the hole, to the space occupied by the vapour in equilibrium with the metal.

---

* *Zeits. f. tech. Phys.*, **11**, 522 (1930).

† See Newman and Searle, " General Properties of Matter," p. 250 (1928).

Proc. Roy. Soc., *A*, **103**, 469 (1923).

Edmondson and Egerton [*] also determined the vapour pressures of sodium and potassium between 100° C. and 200° C. by means of this *effusion method.* Here special difficulties arise from the great reactivity of the alkali metal vapours. Rodebush and de Vries [†] determined the vapour pressure of sodium by means of a similar method.

This effusion formula has also been used by Langmuir [‡] to measure the rates at which highly refractory metals evaporate. If the vapour pressure of any substance does not exceed 1 mm. of mercury, the actual evaporation rate is independent of the pressure around it, or, in other words, the evaporation in a high vacuum takes place at the same rate as it does in the presence of the saturated vapour. When a metal, then, in the solid state is in equilibrium with its own vapour at a pressure p_1, the above equation must give the rate at which the atoms from the vapour strike the surface. On the other hand, at equilibrium, there are just as many atoms evaporating per unit area per unit time as condense. Consequently the preceding equation must give the rate of evaporation of the solid at the temperature T, so that by observing the rate of decrease in weight of a given filament at any temperature T, it is possible to calculate the vapour pressure at that temperature. In this manner Langmuir has measured the vapour pressure of metallic tungsten over the range of temperature from 2,000° K. to 3,540° K., and Langmuir and Mackay [§] have obtained similar data for the metals platinum and molybdenum. These experimenters have also applied the same method to the determination of the vapour pressure of the metals iron, nickel, copper and silver. Born * has determined the vapour pressure of carbon, measuring the loss of weight of a carbon filament.

---

[*] *Proc. Roy. Soc., A*, **113**, 520 (1927).
[†] *Journ. Amer. Chem. Soc.*, **47**, 2,488 (1925).
[‡] *Phys. Rev.*, **2**, 329 (1913).
[§] *Ibid.*, **4**, 377 (1914).

It is assumed that every atom of vapour condenses on striking the metal. If, however, a certain proportion, α, of the atoms of vapour are reflected from the surface, then the vapour pressure will be greater than that calculated in the ratio $1 : (1-\alpha)$. There are good reasons for believing that this reflection from the surface is negligible.

Now when atoms having kinetic energy corresponding to a temperature T_1 strike a surface at a higher temperature T_2, the reflected atoms possess energy corresponding to T_2 only if there is complete equalisation of temperature during the act of impact on the surface. If this is not the case, the atoms leaving the surface have a temperature, T, intermediate between T_1 and T_2 such that :

$$T - T_1 = a\,(T_2 - T_1),$$

or,

$$T = aT_2 + (1 - a)T_1,$$

where a is a number less than unity, which has been designated as the *accommodation coefficient* by Knudsen. On the whole the experimental work on the accommodation coefficient leads to the conclusion that the amount of specular reflection in heat transfer is ordinarily quite negligible, and does not exceed a few per cent.

Mayer † has described a new method for measuring extremely low vapour pressures. The essence of the method lies in having two connecting vessels, in one of which the pressure is that of the vapour to be measured, and in the other is a pressure several hundred times less than that of the vapour, so that the difference in pressure is practically equal to the vapour pressure itself. A tube connects these two vessels, and in front of its opening is a light vane, which is deflected by an amount proportional to the pressure difference. The deflection is practically independent of the temperature and of the nature of the molecules striking the vane. The method is considered suitable for pressures from 10^{-7} to 10^{-2} mm. of mercury.

---

* *Zeits. f. tech. Phys.*, **7**, 24 (1926).

† *Zeits. f. Phys.*, **67**, 240 (1931)

6. Surface Tension and Thin Films. Modern theory suggests that the interface separating two fluids is a special phase, the transition layer at the boundary of two phases consisting of two unimolecular layers, one in each phase.

Evidence as to the nature of the boundary phase has been obtained from experiments involving the spreading of oils and other substances upon the surface of water. So much information is now available as to the dimensions of molecules and the forces about them, much of it being of an accurate quantitative nature, derived from structural organic chemistry, from the study of crystals, the kinetic theory of gases and the deviations from the simple gas laws, *etc.*, that an attempt to deduce the arrangement of the constituent molecules from the properties of the films has become something more than a speculation, and may be made with some certainty and definiteness.

It has been shown by Langmuir * that films do occur which are only one molecule in thickness, such, for example, as the very thin films of oil and other substances on water. If C_1 is the surface concentration in gram-molecules per square centimetre of a unimolecular layer, then the surface area, occupied by a molecule, is $a = 1/C_1N_m$, where N_m is the number of molecules in a gram-molecule. He measured a by dropping a known quantity of oil on water, and stretching this oil film until its measured surface tension changed. This occurred when the film occupied its maximum area, *i.e.*, when it was only 1 molecule thick. His values, calculated for different substances, are in agreement with those found experimentally for insoluble films by X-ray methods. Langmuir used a balance method to measure the excess pull exerted on a paper strip, placed in the surface and separating a pure water surface from one contaminated by a known thickness of oil. This method has been extended by Adam. †

When a drop of some fluid is placed upon a clean water surface, a film of small thickness—about 1 micron (1μ)—rapidly spreads from it in all directions. Hardy,‡ who has investigated the phenomenon, calls this *primary spreading.* In addition, sometimes the drop itself extends into a film of thickness from 50 to 500 microns, which is in tensile equilibrium with the invisible film. The whole may then settle down into an irregular pattern, the apparent spaces of which are occupied by the invisible film. There are thus two distinct processes, the spreading into the very thin film and the extension of the drop into a layer. The latter effect is called *secondary spreading.* Drops of certain fluids of low chemical activity and negligible vapour pressure, such as paraffin, can be placed on a clean water surface without the formation of the film.

---

* *Proc. Nat. Acad. Sci.*, **3**, 251 (1917).

† "The Physics and Chemistry of Surfaces," 1930.

‡ *Proc. Roy. Soc.*, *A*, **88**, 316 (1913).

Hardy placed drops of acetic acid on a glass plate, water vapour being rigorously excluded. Although apparently all of each drop remained in position, there had, in fact, spread from it an invisible film, and the existence of the latter was proved by a measurement of the static friction of the glass surface, before and after the drop had been placed upon it.

Secondary spreading occurs when a drop of acetic acid containing water is placed on a glass plate, and if several drops of the liquid are present on the plate, the existence of the invisible film is manifested in a curious way. Drops which are not more than 1 or 2 centimetres apart attract one another. They become oval in outline, the long axes being directed towards one another, and move slowly across the plate until they meet and coalesce. The invisible film is nowhere greater than 1 micron in thickness, and yet it is capable of pulling larger drops of fluid along.

Now if a drop is to remain on the surface of a liquid without spreading, we must have *:

where S_1, S_2, and S_{12} are, respectively, the surface tensions at the liquid drop-air interface, the liquid (bulk)-air interface, and the interface between the liquid drop and the supporting liquid. If the liquids in equilibrium are completely miscible, S_{12} tends to become zero, and the drop will spread if $S_2 > S_1$. In general, the drop will spread over the surface of the supporting liquid if $S_2 > S_1 + S_{12}$, as, for example, a drop of ether on water. If $S_2 <$

---

* See "General Properties of Matter," Newman and Searle, p. 195 (1928).

$S_1 + S_{12}$, the drop assumes the shape of a lens, forming a re-entrant angle with the liquid. An example of this is a drop of petroleum placed on water. Although S_2 may be greater than $S_1 + S_{12}$, the effect of dissolved substances may result in S_2 decreasing to S_2' and so becoming less than $S_1 + S_{12}$, where S_2' is the surface tension of the contaminated liquid. This occurs with benzene, or oils containing fatty acids, dropped on water.

In other types of spreading the drop does not extend as a homogeneous thin lamina, but undergoes a superficial solution. If the spreading substance is volatile, it may vaporise from the surface of the drop and condense on the clean surface of the supporting liquid. This decreases the free energy of the latter, and we obtain another type of spreading, through the vapour phase, even if $S_2 < S_1 + S_{12}$. For example, carbon disulphide will spread on water by this means.

If a layer of sensible thickness of a pure liquid, such as benzene, is formed on water, and allowed to thin, or evaporate, a sudden rupture occurs when a critical layer thickness is reached, and the benzene collects into a number of flat discs, or lenses. If evaporation is stopped, these lenses will coalesce into a single large lens, surrounded by an area of water covered with a very thin layer of benzene. The liquid underneath is saturated with benzene, so that the vapour pressure above the lens must be identical with that above the thin layer. The formation of such primary layers on water takes place from the drop itself, only when the sum of the tensions of the upper and lower surfaces of the lenticular drop is considerably less than that of water, or,

For example, with oleic acid :

$$74 > 15 + 31.$$

When $S_1 + S_{12}$ is only slightly less than S_2, the drop does not flash over the water surface, but remains apparently unaltered. It is, however, the vapour phase which condenses to form the primary composite surface. Thus, with octane,

$$74 > 20{\cdot}6 + 53.$$

Whether primary, or secondary, spreading does, or does not, occur on a fluid face depends mainly upon the relative values of the surface tensions, but on a clean solid face it must depend wholly upon the vapour tension. If vapour is given off, it will condense to form a primary composite surface, and this, being contractile, may pull the drop itself into a secondary surface. The fact that paraffin and castor oil do not spread at all on clean glass is due to their low vapour tensions, and is no evidence as to the tension of the glass-oil interface.

It has been noted previously, that in the case of the spreading of insoluble oils on water, the thin layer in equilibrium with a lens of an oil, such as oleic acid, is unimolecular in character. Langmuir pointed out that if the molecules in the film are regularly orientated on the surface of the water, owing to the attraction between the latter and the active groups of the organic liquid, such groups as COOH and CH_2OH are dissolved in the water. Long hydrocarbon chains are attached to these groups, and the molecules have no tendency to dissolve, but stand vertically in the surface. There is no particular reason, therefore, for another layer of oil molecules to spread out over the first and form a second layer. Langmuir measured the cross-section and length of the molecules in the surface layer, and showed that in many cases, such as oleic acid, palmitic acid, *etc.*, the length of the molecule is greater than the cross-section, *i.e.*, the molecules are asymmetric. As the chain length increases, the lateral adhesion increases, and the area occupied by two adjacent molecules is reduced. This has been noted experimentally.

Since the films of fatty acids, and the other substances investigated, appear to be only one molecule in thickness, and to have all the molecules arranged in similar orientation—often simply perpendicular to the surface—measurement of the mechanical properties of films, consisting of a known number of molecules of a pure substance, affords unusually direct information concerning the force fields round individual molecules.

Langmuir * brings a great deal of evidence to show that the force fields are the cause of chemical combination, in its widest sense, and of cohesion and surface-tension phenomena. This idea is confirmed in a remarkable manner by his experiments upon thin films of various insoluble fatty acids, esters and alcohols, spread upon water. The molecules of such substances attach themselves to the water by those atomic groups, which exhibit residual polar affinity in the reactions of organic chemistry. This definite localisation of the points of attraction in the molecule produces an orientation ; as stated above, the palmitic acid molecule turns perpendicular to the surface, while oleic acid, being attached by the carboxyl group and also at a point in the middle of the chain, is bent down towards the water at the latter point.

---

* *Loc. cit.*

Recently Adam * has done a great deal of experimental work in connection with films on water surfaces. His apparatus consists essentially of a float of metal foil, paraffined and joined to the side of the trough containing the water by very thin, flexible strips of gold ribbon, placed vertically in the water. By means of a system of torsion wires and an optical lever, the position of the float and the force needed to bring it to any given position are recorded ; in this way the *surface pressure* † is measurable to about 0·01 dyne per cm.

If the molecules comprising the film are not aggregated together into a mass, they form a *gas film* and partake of the thermal agitation of the water molecules, and if they are insoluble, only the two components of translatory movement in the surface can produce displacement of the molecules over considerable distances. If the molecules have an average kinetic energy of translation in each degree of freedom, equal to $\frac{1}{2}RT$, the surface pressure F obeys a perfect gas relation, $FA = RT$. If A is the film-area per molecule in square Ångstrom units, R has the value 1·372 per molecule. At room temperature FA should have a value about

---

* *Loc. cit.* See also Trillat and Nowakowski, *Ann. de Physique*, **15**, 455 (1931).

† If an insoluble and non-volatile substance, which forms a stable film, is spread on the surface of water, it exerts an outward force on a barrier in the surface, provided that the far side of the barrier is in contact with clean water. This force is the *surface pressure*, and is quantitatively equal to the depression of the surface tension by the film. It is a function of the area A of the film.

100. With the insoluble films, values of R approaching to the perfect gas value have not been found at pressures above a few tenths of a dyne; as the area is decreased below about 4,000 square Angstrom units, phenomena analogous to cohesion in gases are found. The isothermals relating F to A, or FA to F, resemble closely the $P - V$ and $PV - P$ curves of vapours in three dimensions. The $FA - F$ curves of Rideal and Schofield,* obtained by using Gibbs's adsorption equation, and those of Adam and Jessop,† using direct measurements of surface pressure, fit exactly; this coincidence constitutes a proof that the adsorbed films are one molecule thick.

When the films are below a critical temperature, the value of which depends on the constitution of the molecules, there is a region of constant surface pressure, apparently analogous to vapour pressure. These vapour pressures are never greater than 0·3 dyne. In the region of constant pressure, the isothermals indicate that there must be two surface phases in equilibrium, liquid and gaseous. The liquid film to which the gas film condenses may be either what is termed the *condensed film*, or the *liquid-expanded film*. In the condensed film the molecules are closely packed and orientated nearly perpendicular to the surface. The liquid-expanded films are more compressible, and have a greater area than the condensed films.

The condensed films are the most closely packed form of films; but a considerable variety of different packings is possible. When the polar group adjacent to the water is small enough, the molecules pack to 20·4 square Angstrom units per molecule under the forces of cohesion alone, without external compression. Condensed films are also found of slightly greater area, in which the polar ends of the molecules alone seem to be in contact. In these films (closely packed heads) the area generally depends on the nature of the head, and is a measure of the maximum cross-section of the end group, as packed in the films. Occasionally the stability of one, or other, packing in the films is dependent on temperature;

---

* *Proc. Roy. Soc.*, *A*, **110**, **167** (**1926**).

† *Loc. cit.* **See also Marcelin,** ***Comptes Rendus*****, 189, 236 (1929).** **Emir,** *ibid.*, **189, 239 (1929) and Guastalla,** ***ibid.*****, 189, 241 (1929).**

there is allotropy, with a transition temperature between the two forms.

Many substances—the amides, fatty acids, bromo-acids and nitriles—condense from the gaseous state of the films into the state of the liquid-expanded film. The latter area is about 48 square Ångstrom units per molecule at no compression; the films are compressible to two-thirds of this area, or less, by forces of the order of 20 dynes per centimetre. The area of the liquid-expanded film of 48 square Ångstrom units does not appear to depend either on the length of the chain, or on the nature of the head; it must therefore be determined by the chain, orientated in such a way that the length does not affect the area. The area of the chain packed as nearly vertical as possible is 20·4 square Ångstrom units. Adam and Jessop * suggested that in the liquid-expanded films, the chains are coiled down in the form of a helix, with axis vertical, the molecules being in contact in this configuration. Later Adam abandoned this theory and postulated that the chains have considerable tilt.

In some cases it does not appear possible for the liquid-expanded film to exist. The effect of rising temperature on these films is to cause the condensed films to change directly into a state which passes later, without discontinuity, into the gaseous film, whereas the liquid-expanded film passes with discontinuity into the gaseous film. The existence of a constant vapour pressure is the criterion for a liquid-expanded film.

The orientation of the molecules in the dilute vapour and gaseous films is probably horizontal, and there is often appreciable delay in reaching the equilibrium packing in condensed films, in some cases as much as five minutes.

Recently, Emir † has studied surface films of oleic acid on mercury. The behaviour is similar to that on a water surface, the phenomenon of saturation being observed. The superficial pressure corresponding to saturation is 60 dynes per cm., or about double that observed on water. The thickness of the saturated film is 24 Ångstrom units, and 23 Ångstrom units has been

---

* *Trans. Farad. Soc.*, **22**, 471 (1926); *ibid.*, **24**, 53 (1928).
† *Comptes Rendus*, **190**, 176 (1930).

observed with water. It appears that in both cases the molecules are in contact at the saturation point, and that the orientation of the molecules is the same on mercury and water.

Another interesting branch of the theory of liquid interfaces is interfacial electrification. Whilst there undoubtedly exists a potential difference at an air-liquid interface, its measurement in absolute units has not yet been achieved. The change in potential produced by the replacement of the liquid surface by a Gibbs's layer of known composition (adsorption of solute molecules to a definite concentration) can be readily ascertained.* This alteration in the potential difference is caused by the replacement of a free, and possibly orientated, water surface possessing an electric moment, by one containing orientated solute molecules. Not only can solute molecules alter the interfacial potential difference by orientation, but ions can effect similar results. Thus, in the case of a mercury-electrolyte interface (capillary electrometer) the charge on the mercury surface will cause an ionic distribution to be set up in the neighbouring solution, which has an equal and opposite charge. Helmholtz † was of opinion that this simply consisted of a layer of ions of sign opposite to that of the surface charge, and in number sufficient exactly to neutralise it. Schofield ‡ has found, however, that when a negatively-charged mercury surface is in contact with a sodium chloride solution, chloride ions are in deficit at the interface. Such a deficit is to be expected on a theory put forward by Gouy § in which the volume electrification set up extends some distance from the mercury surface and is due, partly, to an accumulation of ions, carrying a charge opposite in sign to that on the surface, which are attracted to it, and partly to a deficit of ions, carrying the same sign of charge as the surface, which are repelled from it. To satisfy experimental data, however, this *diffuse double-layer* of Gouy must be replaced by a composite double-layer of a type originally suggested by Stern,‖ and consisting of one of the Helmholtz type

* See Frumkin, *Zeits. phys. Chem.*, **116**, 485 (1925).
† "Physical Memoirs," 1888.
‡ *Trans. Farad. Soc.*, **22**, 455 (1926).
§ *Ann. de Physique*, **7**, 129 (1917).
‖ *Zeits. Elektroc.*, **30**, 508 (1924)

and outside this, a diffuse layer. It is unlikely that the *condensed* Helmholtz-type layer is more than about 4 Ångstrom units thick at a water-mercury interface, otherwise it would interfere with the diffuse layer. Hence the effective dielectric constant of whatever separates the charges on these ions from those on the surface cannot be 80 (specific inductive capacity of water), since in this case the thickness would be about 40 Ångstrom units. Neither can it be unity, as the charges would then be separated by only 0·5 Ångstrom unit, which is less than an atomic diameter. Stern supposes the necessary dielectric constant, of value 4 to 8, to be that of the ion itself, but it seems more probable that the charges are separated by a layer of water molecules, which, owing to the intense fields, are approaching dielectric saturation, *i.e.*, complete orientation.

In the diffuse layer the force which causes the volume electrification is the charge on the surface of the metal or rather, the charge on the surface of the metal, less that on the ions in the condensed layer. But from a study of electrocapillary curves, like those for KI, it is evident that another force may come into play in the condensed layer, for iodide ions form a condensed layer when the potential difference across the interface is zero, or even negative (mercury negative with respect to solution), in which case the electrical forces are driving them from the surfaces. This is evidently a case of selective ionic adsorption, in which an ion is held to the surface by a chemical, or quasi-chemical, force, and indicates how a complex ionic layer may be built up on a non-conductor.

Gouy * showed that the shift in the position of the maximum of the electrocapillary curve, caused by the presence of capillary active organic substances, is proof that the molecules adsorbed at the mercury surface affect the *electric moment of the interface*.† Frumkin's ‡ measurements of the changes in the total potential difference at a water-air interface, caused by spreading a unimolecular film of an insoluble fatty acid over the surface, indicate that the addition of each orientated COOH-group changes the electric moment of the interface by an amount which is only slightly dependent on the number of molecules already present, per unit area of surface. The change in moment produced by each molecule cannot be identified with the electric moment of the molecule itself, as besides displacing water molecules, which may themselves have contributed to the interfacial moment, each fatty acid molecule will, by its presence, lead to changes in the effective moments of surrounding molecules, and also cause a redistribution of neighbouring ions. Since these films may alter the potential difference across the interface by half a volt, in some cases, it is clear that molecular orientation is an important factor in contributing to the electric moments at interfaces.

---

* *Loc. cit.*

† By considering the average volume charge in a lamina, no lower limit need be set to its thickness. It is thus possible to speak of ρ, the volume density of electricity in a lamina of infinitesimal thickness dx, and to evaluate $M = \int \rho x dx$, the electric moment of the interface.

‡ *Loc. cit.*

It has been shown that many organic molecules lower the surface tension by reason of a two-dimensional kinetic bombardment pressure. Though the molecules have a moment, they do not appear to repel one another appreciably on this account. The effect of an ion, and its complementary charge, on the interfacial moment is approximately ten times that of a fatty acid molecule. Since the lateral repulsion of the ions depends on the square of the moment, it may be a hundred times greater than that due to organic molecules. Thus, we find a surface-tension lowering of some 60 dynes per cm. for 10^{-10} gram-ion per sq. cm. (the lowering of the surface tension by many organic molecules approximates to 2·4 dynes per cm. for a surface concentration of 10^{-10} gram-molecule per sq. cm.). In the case of ion-adsorption the surface-tension lowering varies approximately as the square of the surface concentration, which is to be expected if it is mainly due to doublet repulsion, as the latter varies inversely as the fourth power of the distance, *i.e.*, inversely as the square of the area occupied by each doublet. In this transition from adsorption of polar molecules to adsorption of ions the purely electrical effects thus increase in magnitude, as is to be anticipated from the increasing value of the electric moment. Even in the extreme cases of completely dissociated electrolytes, however, the chemical adhesion is one of the most important factors.

Frumkin * obtained the approximate value of 0·4 volt for the difference between the total potential difference at air-water and air-alcohol interfaces, and this difference showed no signs of dropping to zero in the absence of an electrolyte. It thus appears that in this case the difference in total potential difference is mainly due to a substitution of orientated alcohol molecules for water molecules in the surface layer, an idea which is supported by the fact that ethyl and methyl alcohols have almost the same interfacial potential difference against air. When electrolytes are present, an ionic distribution is set up in the neighbourhood of the surface which gives rise to electrokinetic phenomena, but which makes only a small contribution to the total potential difference.

It appears that there is no essential difference between electrical and chemical adsorption. Kar and Ganguli † assumed that the adsorption of ions occurs independently of one another and that in the case of positive and negative ions both electrical and chemical adsorption take place simultaneously, although for a given ion either electrical or chemical adsorption predominates. From these assumptions a formula is developed which gives the relation between the concentration of the ions and the amounts adsorbed.

Very recently a new type of method has been developed for the examination of surface films. Schulman and Rideal ‡ measured the potential difference between a platinum wire situated above the surface of a glass trough and a calomel electrode, establishing contact with the liquid in the trough. A small quantity of polonium was electrodeposited on the platinum wire. With this apparatus reproducible air-liquid potential differences could be obtained, independent, within relatively wide limits, of the distance of the polonium-coated wire above the surface of the liquid in the trough.

Joffé and Lukirsky § have also measured the potential fall at a molecular layer of stearic acid on a gold plate by means of

---

* *Zeits. phys. Chem.*, **111, 190** (1924).
† *Zeits. f. Phys.*, **61**, 411 (1930).
‡ Cambridge, *Phil. Soc. Proc.*, **26**, 273 (1930).
§ *Journ. de Phys. et le Radium*, **1**, 405 (1930).

ionisation caused by polonium placed at a suitable distance therefrom. From their results they conclude that in the first layer the molecules of stearic acid are all attached to the plate by the same end of the chain, or by opposite ends, according as the plate is alkaline, or acid, the next layer is attached to the first in the opposite way, while the third is arranged as the first.

7. Adsorption on Solids. Adsorbed molecules on solids are also orientated. Evidence of this molecular orientation by surface is available from the work of Hardy[*] on lubrication, from the behaviour of crystalline liquids at plane surfaces,[†] and in the mode of crystallisation of long-chain acids on the surface of mica.[‡] Constable and Palmer[§] have also shown that the temperature coefficient of the reaction for different alcohols is constant. This, they explain, as due to the group on the surface, CH_2OH, being adsorbed by the surface in all cases.

The formation of monomolecular films on adsorption from solution has been observed by numerous workers, and definite evidence has been obtained by Bartell and Miller[‖] that with organic polar compounds orientation on a carbon surface occurs from solution. They conclude that the polar groups are extended into the water phase, and that the hydrocarbon is directly in contact with the surface.

When we compare the results of X-ray work with those obtained by a study of thin films as above, we see that there is a close relation between the type of orientation found in molecular aggregates, other than solids, and that which is the principal characteristic of the crystal. The study of films of long chain compounds shows that they very readily form layers in which the molecules are arranged side by side, parallel to one another. Adam's measurements of the cross-section of the molecules in close-packed films agree with those determined by X-ray work.

The arrangement of molecules in an orientated film is a replica, more or less perfect, of crystalline structure. X-ray measurements

---

[*] *Phil. Trans.*, *A*, **230**, **1**, (**1931**).

[†] See Friedel, *Ann. de Physique*, **18**, **273** (**1922**).

[‡] See Muller and Shearer, *Journ. Chem. Soc.*, **123**, **2043**, 3152 (1923).

[§] *Proc. Roy. Soc.*, *A*, **107**, **255** (**1925**).

[‖] *Journ. Phys. C*

have shown that in crystals of these long-chain compounds, *i.e.*, *substances* whose molecules are based on a long open chain of carbon atoms, there is one set of planes whose distance apart is very much greater than that of any of the other planes. Further, the value of this spacing increases uniformly as the carbon content of the molecule is increased. This at once suggests that the spacing is closely connected with the length of the molecule, and confirms the chemical deduction that the carbon atoms are arranged in chain fashion. For a given carbon content, the actual value of the spacing approximates to one or other of two values, one of which is just double the other, *i.e.*, the rate of increase per CH_2 group is twice as great as in the other. This suggests that in one case we have to deal with an arrangement in which successive identical planes are separated by a single layer of molecules while in the other there is a double layer. Results show that if the molecule has, at one end, a group which is chemically active, *e.g.*, COOH, then the double layer will be found ; if both ends are inactive, as in the hydrocarbons, only a single layer will occur. As it appears to be the active groups which result in the formation of the double layer, the natural conclusion is that the two layers are oppositely orientated, the active groups of the bottom layer being directed towards the active groups of the upper layer.

The double and single layers which we find in these long chain crystals have probably a considerable bearing on the possibility of the formation of orientated films. Generally speaking, it would appear that those substances which form into crystals with double molecular layers are those which readily give rise to highly orientated films. The film of, say, stearic acid on water, although of monomolecular thickness, should preferably be considered as a double layer of orientated molecules, the one layer being acid, the other water, with their active groups orientated towards one another.

X-ray examination shows that in cases where a double layer is formed, the outer ends of the double layer are always the inactive groups. In the case of a crystal of stearic acid, for example, the groups which appear on any cleavage plane of the crystal are CH_3

and never carboxyl groups. This fact seems to be of some significance in connection with Hardy's lubrication experiments.* He suggests that in the limiting case, there is, between the two sliding surfaces, a double layer of molecules of lubricant, one layer being attached to each surface, and the sliding taking place between the two layers. It seems rather improbable that a set of COOH groups will slide easily over another set, so that if the molecules are standing up from the surfaces, their carboxyl groups must be attached to the surfaces. X-ray measurements, on the other hand, show that the carboxyl groups have a strong tendency to come together. Either the attractions of the various surfaces, used in the experiments, for the carboxyl group are very much greater than the attractions of the carboxyl groups for one another, or the true explanation of the phenomenon is that the type of molecular orientation, under the conditions of these experiments, is different from that found in the case of films of stearic acid on water.

Pure liquids give X-ray diffraction bands,† which suggests that in the body of a pure liquid there exist small groups of orientated molecules, so it appears that any attempt at orientation is essentially an attempt at crystallisation.

8. Viscosity of Liquids. The study of the viscosity of liquids has in the past consisted largely of a collection of more or less well established empirical relations. There was, until recently, no general theoretical basis for the subject, *e.g.*, no physical mechanism had been put forward to account for the decrease of liquid viscosity with temperature, in contrast to the familiar and well explained increase of gaseous viscosity with temperature. Many empirical formulæ ‡ have been proposed to represent the variation of liquid viscosity with temperature, but they have all at least three arbitrary constants and a very limited range of validity. Recently, renewed interest has been created in the subject, and Andrade § has given a general account of the influence of temperature on liquid viscosity. In addition, he has deduced a simple formula which fits the experimental facts very well. The formula is:

---

* *Proc. Roy. Soc.*, *A*, **104**, 25 (1923).

† See Keesom and Smedt, *Proc. Acad. Sci.*, Amsterdam, **26**, 112 (1923).

‡ See Hatschek's "The Viscosity of Liquids."

§ *Nature*, **125**, 309, 580 (1930)

where η is the coefficient of viscosity, T, the absolute temperature and A and b, constants. It holds over practically the whole temperature range with a great variety of substances. A test of the formula is provided by Porter's general viscosity relation, which states that if two liquids be examined throughout a sufficient range of temperature, a number of temperatures T_1, can generally be found for one liquid (I.) at which the viscosity is the same as it is for the other liquid (II.) at a number of temperatures T_2. If T_1/T_2 is plotted against T_1, a straight line results.

This relation follows at once from Andrade's formula. For if A_1, b_1 and A_2, b_2 are the constants for liquids (I.) and (II.), then:

$$A_1 e^{b_1/T_1} = A_2 e^{b_2/T_2},$$

so that,

$$\log \frac{A_1}{A_2} = \mathit{constant},$$

for the two liquids concerned and also:

$$\log \frac{A_1}{A_2} = \frac{b_2}{T_2} - \frac{b_1}{T_1},$$

or,

$$T_1/T_2 = \alpha + \beta T_1,$$

where α and β are constants. This is the experimental relationship.

Andrade, in arriving at his formula, takes two layers of molecules parallel to the direction of motion of the liquid, and considers the transfer of momentum between them. He supposes that the momentum is transferred from layer to layer by a temporary union of molecules in contiguous layers, the duration of this union not exceeding the very brief time required for the molecules to acquire a common velocity of translation. The union takes place under the action of the residual field of the molecules, which suffices to bind them permanently in the solid state, but is overcome by the energy of motion in the liquid state. General considerations suffice to show that the greater the temperature agitation, the smaller the probability that the residual field of fixed average strength will result in temporary union for a given molecule. The viscosity of a liquid, therefore, decreases with rise in temperature until finally the energy of motion overcomes the molecular field and the liquid boils. The general picture is one of the liquid "crystallising" temporarily in minute patches; at the temperature of solidification, the crystallisation becomes general and permanent; at the boiling point, it must be very small.

Andrade next supposes that the temporary combination represents the position of minimum potential energy of the molecule with respect to the local field, the tendency of two molecules to combine being opposed by the thermal agitation. Then the constant b is of the form $-E/k$, where E is the energy, numerically negative, of juxtaposition and k, the Boltzmann constant.

The constant A may be taken to a first approximation as independent of temperature and contains as factors $M^{3/2}\rho^{-1/3}$, where M is the molecular weight and ρ, the density. The formula for viscosity virtually assumes that the number of impacts is independent of the temperature, the effect of the increased velocity being opposed by certain factors, such as the expansion.

Andrade distinguishes between true association, as occurring in liquids ordinarily called associated, and the brief union needed for the sharing of momentum postulated for all liquids. True association, in which the molecules are bound together in clusters of two, or more, for a time large compared to the intervals between collisions, leads, with the mechanism postulated, to an increase of viscosity.

In the case of water the formula $\eta = Ae^{b/T}$ expresses the viscosity coefficient within 0·5 per cent. from 100° to 60° C., when the deviation begins to set in and rapidly increases.

For water and other associating liquids a formula of the type:

is also appropriate, the term $(1 + \alpha e^{-\beta T})$ expressing the decrease of association with temperature. This formula has four constants, but four constants are commonly used in empirical formula designed to fit water. It gives the coefficient of viscosity over the range, $T = 263{\cdot}7°$ (supercooling of 9° C.) to $T = 363°$, within 0·25 per cent.

Among other formulæ which have recently been proposed to represent the variation of viscosity with temperature may be mentioned the following :

Madge * finds that the formula :

holds for a number of liquids over a wide temperature range, such liquids including both normal and associating ones. The formula has three constants, but is similar to that of Andrade's in that it contains an exponential function. From general molecular theory and in view of the direct relation between viscosity and vapour pressure, it is probable that an exponential form of equation for viscosity and temperature will prove to be most satisfactory.

Black † has pointed out that Andrade's formula does not give such good agreement when applied to measurements on some mineral oils as does the formula :

$$\eta = \frac{C}{t + a}n,$$

where t is the temperature in °C. and C, a and n, constants depending on the liquid used. The value of C, obtained from eight oils of widely varying viscosities, can be expressed with considerable accuracy by the formula :

$$C = ad^n,$$

where a and d are constants, which are independent of the nature of the oil and the approximate values of which are $1{\cdot}5 \times 10^{-3}$ and 400, respectively.

Sheppard ‡ has independently put forward a formula similar to that of Andrade's.

---

* *Nature*, **130**, 580 (1930) ; see also *Journ. Phys. Chem.*, **34**, 1599 (1930).

† *Nature*, **130**, 581 (1930).

‡ *Ibid.*, 489 (1930).

BIBLIOGRAPHY

ADAM. "The Physics and Chemistry of Surfaces."
BRIDGMAN. "The Physics of High Pressures."
DUSHMAN. "High Vacuum."
KAYE. "High Vacua."
NEWMAN. "The Production and Measurement of Low Pressures."
NEWMAN and SEARLE. "The General Properties of Matter."

CHAPTER IV

ACOUSTICS

DURING the past ten years the development of acoustics, particularly as regards the new methods of investigation, has been most marked. On the one hand, the range of frequencies with which the subject was formerly concerned has extended into regions beyond audition—into the *supersonic region*, *i.e.*, the region of very high frequencies, and also into that of very low frequency air pulses. On the other hand, acoustics has extended into a new area—the so-called *electro-acoustics*, which is based on the telephone and loud speaker, and the study of acoustics is now most keenly pursued, not for its intrinsic scientific interest alone, but also because of its utilisable results.*

1. Velocity of Sound in Liquids. From a practical point of view, the most interesting liquid in which the velocity of sound has been measured recently is sea-water. Accurate measurements of the velocity of sound in the sea are imperative because of the various methods, which are now in use, to measure depths and distances in the sea.

Wood, Browne and Cochrane † carried out an extensive series of velocity measurements off Dover. Four hydrophones ‡ were fixed at intervals of about four miles on a base line running approximately north and south, the positions of these hydrophones being known to within one part in 10,000 of the total base line. Each instrument was connected by cable to a string in an Einthoven galvanometer ; a fifth string was operated by the half-second ticks of a chronometer, while a sixth string recorded a wireless signal sent from a destroyer at the instant a depth charge was fired.

---

* An admirable and stimulating review of modern acoustics is given by Eccles in the *Proceedings of the Physical Society*, 41, 231 (1929). See also a report on Audition, *Proc. Phys. Soc.*, (1931).

† *Proc. Roy. Soc.*, *A*, 103, 284 (1923).

‡ A hydrophone is an under-water microphone.

The impulses recorded by the strings were photographed on a slowly moving film, which was developed and fixed automatically. The photographic record was crossed by a series of fine lines, marking seconds, tenths and hundredths—for very accurate work thousandths of seconds could be estimated. These time marks were made by means of a phonic wheel, controlled by an electrically maintained tuning fork.

During the velocity measurements, continuous observations were made of the sea conditions, *i.e.*, temperatures and salinities, and corrections applied, if necessary, for tidal flow. Preliminary investigations had shown that the velocity was independent of the amount of the explosive charge, within the limits 2·25–300 lb., and that there was no certain variation of velocity with the depth of the charge, 10 to 108 feet. To eliminate the error due to the uncertainty of the position of the charge in an east and west direction with respect to the base line (north to south), a multiple-charge method was employed. About ten small charges were fired at approximately equal time-intervals, and equal distance intervals, along a line perpendicular to the prolongation of the base lines of the hydrophones. The recorded time interval between the reception of the sound by a pair of hydrophones was a maximum for that charge fired nearest in line with the hydrophones, and for the charge fired from a position on either side of the base line, the recorded time interval was less. A curve was then obtained, showing the relation between the time interval and the number of the charge fired, and from this curve the maximum time interval, corresponding to the passage of the sound from one hydrophone to the adjacent one, could be determined. In one particular case the distance between adjacent hydrophones was 70,245 ± 7 feet, and the maximum time interval, 14·176 ± 0·001 seconds. From these results the velocity of sound in the sea is 4,955·4 ± 1 ft. per sec., corresponding to a mean temperature on the base line of 16·95° C. and a salinity 35·02 per cent. The results of the complete investigation gave for the velocity of sound in the sea :

$$4{,}626 + 13{\cdot}8\,t - 0{\cdot}12t^2 + 3{\cdot}73\,S \text{ feet per sec.,}$$

or,

$$1{,}410 + 4{\cdot}21\,t - 0{\cdot}037t^2 + 1{\cdot}14\,S \text{ metres per sec.,}$$

t being the temperature in °C., and S, the salinity in parts per thousand.

Stephenson [*] found the velocity of sound to be 1,453 metres per second, over a distance of about 15,500 metres, through the waters of Block Island Sound, New York, at 0·3° C. He determined the time for the sound wave, produced by the explosion of a bomb, to travel to each of five hydrophones, anchored at widely separated points, and the distance travelled in each case. The depth varied from 18 to over 50 metres. The results from the five independent determinations for each of four bombs were all within ± 0·2 per cent. of the average.

Although the velocity of sound through the sea varies little with the depth for small depths, it is evident that in the oceans, where the depth may exceed four miles, the velocity in such regions must differ appreciably in value from that near the surface. This factor is important in depth measurements. Both the elasticity and the density of the water vary with the pressure, the elasticity increasing more rapidly than the density. Mathews [†] has calculated values of the elasticity, density and velocity at depths varying from 0 to 30,000 feet, the pressure at the latter limit reaching 1,000 atmospheres, and the velocity increasing by 160 metres per second above its value near the surface.

Heck and Service,[‡] using an echo method,[§] measured the variation of velocity with depth for depths ranging from a few fathoms to 4,500 fathoms. There was close agreement between observed and calculated velocities.

Conditions in the sea are much more consistent than they are in the atmosphere, but although the temperature gradients, for example, in the sea are less than in the atmosphere, they become important under certain conditions. Such gradients cause refraction of the sound ray, upwards or downwards, according to the sign of the temperature gradient, the ray being multiply-reflected from the bed, and surface, of the sea. The vertical spreading is thus restricted, and as the absorption in water is less than in the atmosphere, greater ranges are obtainable in the sea for an expenditure of a given amount of power than are obtained in the atmosphere. For example, the sounds of the propellers of a large vessel may sometimes be heard at eight or ten miles away from the boat, but the range of audibility depends upon the state of the sea, *i.e.*, the presence, or absence, of breaking waves, *etc.* It is also probable that the presence of suspended air-bubbles in the water greatly decreases this range.

---

[*] *Phys. Rev.*, **21**, 181 (1923).

[†] "Dictionary of Applied Physics," **3**, 665 (1923).

[‡] U.S. Coast and Geodetic Survey, No. 108 (1924).

[§] See Section 9.

Lichte * has found that the range of transmission of under-water signals varies according to the season of the year. This fact he attributes to the refraction produced by temperature gradients in horizontal layers of the sea.

Lubeke † noted that the velocity increases by 0·2 per cent. for 1° C. rise in temperature, 0·11 per cent. for 100 metres increase in depth, and 0·1 per cent. for 1 per cent. increase in salinity. As the sound travels into deeper water, the velocity first decreases owing to the fall of temperature, and afterwards increases on account of increase of pressure. Omitting the coldest and warmest seas, an average velocity for all depths is found to be 1,496 metres per sec., and an international average of 1,500 metres per sec. is suggested for navigational purposes.

2. Explosive Sounds of Long Range. Explosion sounds, such as those heard when the shell is fired from a gun, give rise to pressure waves of large amplitude, which can be detected, either by the ear or some suitable apparatus, at long ranges. The ejection of the shell from the gun produces waves of low frequency, often referred to as *infra-sounds*, so that an observer at some distance from the gun detects what seems to be a continuous train of waves, due to the numerous reflections of the pulse from objects in its track. Near the source the velocity is high, and the wave form changes as the wave progresses.

A curious effect connected with these large explosions in air is the existence of *zones of silence*. For example, when a large charge is exploded, the sound is heard up to a distance of 60 miles, approximately, and again beyond 100 miles, but not within the range from 60 to 100 miles. The direct wave travelling along the earth's surface is steadily attenuated, the amplitude decreasing so much that at a distance of 60 miles, or so, the sound cannot be detected. Beyond 100 miles the sound is received *viâ* the higher atmosphere, the waves being reflected, or refracted, so that they finally take a downward path to the ground. Whether this downcoming wave is due to reflection from a layer of the stratosphere, 30 km. from the ground, or whether it is due to refraction brought about by air currents and temperature gradients, is still open to discussion, but the effect is undoubtedly due to meteorological conditions.

---

* See "Unterwasserschalltechnik," Berlin

† *Zeits. f. techn. P*

Systematic research on the propagation of air waves is now being carried out in Germany and England. In Germany, explosions produced for the purpose are utilised, while in England use is being made of gunfire, the reception of the sound being recorded by means of the Tucker hot-wire microphone. This consists of a Helmholtz resonator in the neck of which is mounted an electrically-heated grid of fine platinum wire, which forms one arm of a Wheatstone bridge. The resistance of the hot wire is a function of the magnitude of the aerial vibrations in the neck of the resonator. A string galvanometer records the reception of the sound at the grid, and records from several microphones can be made on one moving strip of photographic paper. By multiplying the records in this manner, it can be demonstrated that the waves are coming from the right direction, and also the angle of descent of the waves can be determined.

When the angle of descent is known, as well as the time of passage of the waves over a known distance and the conditions prevailing in the lower atmosphere up to the height reached by the waves, it is possible to determine with fair accuracy the trajectory of the air waves. The velocity of the wave at the highest point is given by the simple formula,*

$$v = v_0 \sec a,$$

where v is the required velocity, v_0, the velocity of the wave at ground level and a, the angle of descent.

---

* See Whipple, *Ger. Beitr. z. Geophys.*, **24**, 72 (1929).

In England there are six observation stations, *viz.*, Birmingham, Bristol, Cardiff, Exeter, Nottingham, and Sheffield, but we have not been successful so far at Exeter in detecting these long-range waves. Although reception has been obtained at the other five stations in summer, no certain reception has been recorded during the winter months. The gun fire origin in the past has been at Shoeburyness, Yantlet or Woolwich. In one particular case the air waves should have taken 615 seconds to pass from Yantlet to Birmingham, whereas the recorded time of passage was 711 seconds, due to the passage of the waves up into the atmosphere and down again to the recording station.

In another record at Birmingham the angle of descent of the waves originating at Yantlet was estimated to be 16°, the apparent velocity of the waves along the ground being 355 metres per second, so that from the property of the trajectory of the waves we deduce that this was the velocity of the air-waves at some height in the atmosphere. Now the temperature corresponding to a velocity of 355 metres in still air is 106° F. If the air had a velocity of 20 metres per second from south-east, the relative wave velocity was only 335 metres per second and the temperature 45° F. The return of the waves to the earth can be accounted for entirely by wind, supposing the temperature to be that of the stratosphere, −58° F., if we postulate the wind velocity to be 56 metres per second. The turning point of the waves was estimated to be 45 km. above the ground. On the same day the angle of descent at Bristol was 27·5°, corresponding to a turning-point height of 55 km.

Another recording instrument is the undograph, which is extensively used in Germany. A steel fibre is fastened to a thin mica sheet along an axis of symmetry, and is arranged to act as a taut suspension. The sheet swings freely, one half, with as little clearance as possible, in an opening through the wall of a large air-tight box; the other half swings in a small chamber, providing some damping, but is protected from the incoming wave. The motion is shown by a beam of light reflected from a mirror on the mica, and the optical, mechanical, and photographic arrangements for recording this, along with the necessary time marker, are all contained inside the box. The natural period of the system is of the order of a second, and the records obtained from waves just below the audible limit are very good, and easily distinguishable from accidental and wind disturbances because they are, approximately, sinusoidal.

A large body of observations has resulted from great activity in Germany, culminating in a systematic series of experiments under the Notgemeinschaft der Deutschen Wissenschaft. Early results indicated a marked seasonal effect, the minimum distance at which sound was heard in the outer zone being 110 km. in winter, and 190 km. in summer. Corresponding distances for maximum intensity were 125 km. and 230 km. The later results followed a searching investigation of the effect on the consistency of the observations of kind and amount of explosive, its position with respect to the ground, the nature of the soil, and methods of detonation. The velocity for the inner zone of audibility is normal for the temperature of the air at the ground, 330–340 metres per second, but the apparent velocity for the outer zone is lower than this, 280–300 metres per second. The conclusion is that the sound in the latter case has traversed a much longer path, *i.e.*, through the upper atmosphere. In different directions from the source of the wave, the time of travel to the same distance in the outer zone varies by as much as 35 seconds.

Several theories have been put forward to account for the existence of one or more zones of abnormal audibility. The effect was at first ascribed to strong winds in the stratosphere, but as soon as it was established that waves were received in all directions, this idea was abandoned as untenable. It was next suggested that the increase in velocity was due to a settling out of the heavier gases and the relative preponderance of hydrogen and helium at the heights where bending takes place. From other considerations, however, it seems unlikely that there is much change in composition below 80–100 km. Even if 25 per cent. of the lighter gases were possible at 50 km., the time of travel is not sufficient for the wave to reach the necessary height, and also the diminution of intensity would be too great in passing through regions of such low pressures.

The ordinary formula for the velocity of sound in a gas is valid only if the amplitude of the wave is small in comparison with the total pressure. If this is not so, the values are much greater, and in the immediate vicinity of explosions, velocities as great as 900 metres per second have been observed. It has been claimed that the velocity increase in the upper regions is due to such a breakdown of the ordinary formula, but it is doubtful whether the total pressure falls off more rapidly with height than the amplitude decreases with distance from the source, when the smallness of the average angle of descent is considered. The supposition that above 30 km. the temperature of the atmosphere increases again with height until it reaches, or even surpasses, ground temperature, is sufficient in itself to account for the abnormal zone of audibility. The above-mentioned velocity of 340 metres per second at 40 km. indicates a temperature thereat of about 15° C. Such high temperatures in the upper atmosphere were first indicated by a study of meteors, and it has recently been shown * that the absorption of solar energy in the ozone layer (centre of gravity about 45–50 km.) is responsible for their maintenance. This explanation, supported as it is by evidence from two independent sources, seems likely to remain as the most important in the field.

Records of explosions in Germany have been obtained at Könisberg at the great distance of 578 km. from the source.

3. High-Frequency Vibrations. Certain crystals, including tourmaline, Rochelle salt and quartz, exhibit electrical charges at particular regions when subjected to stresses, this effect being known as *piezo-electricity*. In all cases the crystals lack symmetry. The converse piezo-electrical phenomenon consists of a mechanical strain produced in a crystal when suitably electrified. Thus, a plate, or rod, suitably prepared from a crystal which shows the piezo-electric effect, and provided with metallic coatings, can be brought into a state of vigorous resonant longitudinal vibration, when the coatings are connected to some source of alternating electromotive force of the right frequency.

Owing to its unrivalled mechanical properties, quartz has thus far been found the most suitable material, though its piezo-electric effect is less than that of tourmaline, and far below that of Rochelle salt. On account of the occasional occurrence of twinning, and possibly other causes, not all quartz crystals are equally good.

---

* See Gowan, *Ger. Beitr. z. Geophys.*, 34, 50 (1929).

The main features of the piezo-electric action may be summarised as follows: Plates are cut from the natural crystal of quartz with the orientation as shown * in Fig. 14. After the natural crystal has been trued up by crosswise cuts, so as to form a prism, with the hexagonal ends, A B C D E F and A′ B′ C′ . . . F′, which are respectively perpendicular to the natural edges AA′, BB′ of the crystal, a rectangular slab is obtained from the prism by two parallel cuts P and Q, which are perpendicular to a natural face, such as ABB′A′.

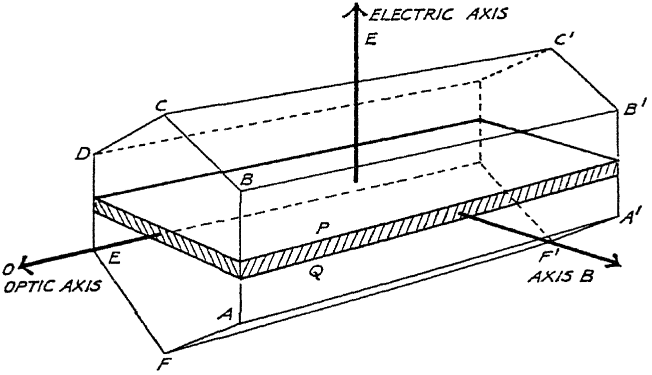


FIG. 14.—Orientation of axes in a natural quartz crystal.

The rectangular slab so obtained has three axes represented in the diagram by arrows; the optic axis O (parallel to the lengthwise natural edges of the crystal), the electric axis E (parallel to two opposite natural faces of the crystal) and the third axis B (perpendicular both to the optic axis and the electric axis). Let l be the length parallel to axis B, b, the breadth parallel to the optic

---

* See Pierce, *Proc. Amer. Acad. Arts and Sci.*, **60**, 271 (1925).

axis O and e, the thickness parallel to the electrical axis E. When such a plate is placed between parallel plates of metal, so that the electric field is parallel to the electrical axis E of the quartz, an elongation in the B direction and a contraction in the E direction, or the reverse, tend to occur, according to the direction of the electric field. These two piezo-electric effects in the B and E directions are called the *transverse* and *longitudinal* effects, respectively. In general, the deformation of a crystal, when in an electric field, is known as the converse effect, the term direct effect being applied to the generation of an electric field in a crystal when mechanically deformed.

If the electric field between the so-formed condenser plates is alternating, the plate vibrates under the impressed piezo-electric stresses with a frequency equal to that of the impressed field. This frequency may, of course, be that of one of the natural modes of vibration of the plate. The modes that are of chief importance in quartz are longitudinal vibrations; *i.e.*, stationary compressional waves in the B, or E, direction. Any given plate possesses a fundamental frequency of vibration in each of these directions, together with overtones which are very nearly in harmonic relation to the fundamentals. In addition, other modes of vibration are nearly always present, and are sometimes a source of annoyance, particularly with the longitudinal effect (E direction). By making use of the transverse effect (longitudinal vibrations in the B direction) in narrow rods, these troublesome nondescript modes of vibration can easily be eliminated, at least in so far as the fundamental and the first few overtones are concerned.

The relation between wave-length and frequency of longitudinal vibration in any direction in quartz may be calculated from the density and Young's modulus. The density, ρ, of quartz is 2·654, and Young's modulus, Y, for extensions parallel to either the E or B axis, is about 8×10^{11} dynes per sq. cm. Hence for the velocity, v, of compressional waves for either the longitudinal, or the transverse, effect we have:

$$v = \sqrt{\frac{Y}{\rho}} = 5{\cdot}5 \times 10^{5} \text{ cm. per sec.}$$

From this, the wave-length, λ, of the waves in the crystal is given by:

$$\lambda = \frac{5{,}500}{f},$$

approximately, where f is the frequency in kilocycles per second, and λ is measured in millimetres. If the boundary surfaces of the plate are free, the fundamental vibration has a node at the centre of the plate, so that l is a half wave-length for the transverse effect, and e, a half wave-length for the longitudinal effect.

For the fundamental frequency we have, on substituting $2e$ or $2l$ for λ in the above equation,

$$f = \frac{2{,}750}{l},$$

for the transverse effect, and,

$$f = \frac{2{,}750}{e},$$

for the longitudinal effect, l and e being the length and thickness, respectively, of the plate, in millimetres.

It is sometimes convenient to express l and e in terms of the wave-length of electromagnetic waves in air. From the equations above it is seen that the dimension of the crystal in millimetres, measured in the direction of vibration, is slightly less than one hundredth of the wavelength in metres, since the latter equals $3 \times 10^8/f$. In other words, about 110 metres of electromagnetic wave-length may be allowed for each millimetre of the crystal in the direction in which vibrations, of the type described above, occur. Thus, a plate 20 cm. long and 1 mm. thick will resonate longitudinally (with respect to the electric field) under an impressed wave-length of about 110 metres, and transversely, when the impressed wave-length is about 2,200 metres.

Cady * showed that a quartz plate, mounted as explained above, with two pairs of electrodes—one to be connected with the first grid circuit of an electric oscillating circuit, and the other to the last plate circuit of an amplifier, with resistance coupling between

---

* *Proc. Inst. Radio Eng.*, **10**, 83 (1922).

stages—is capable of giving sustained oscillations with a period fixed by the mechanical period of the quartz alone. The reactions of such a resonator upon a high-frequency circuit are fully accounted for, consisting as they do of characteristic changes in the effective capacity and resistance of the resonator, as the

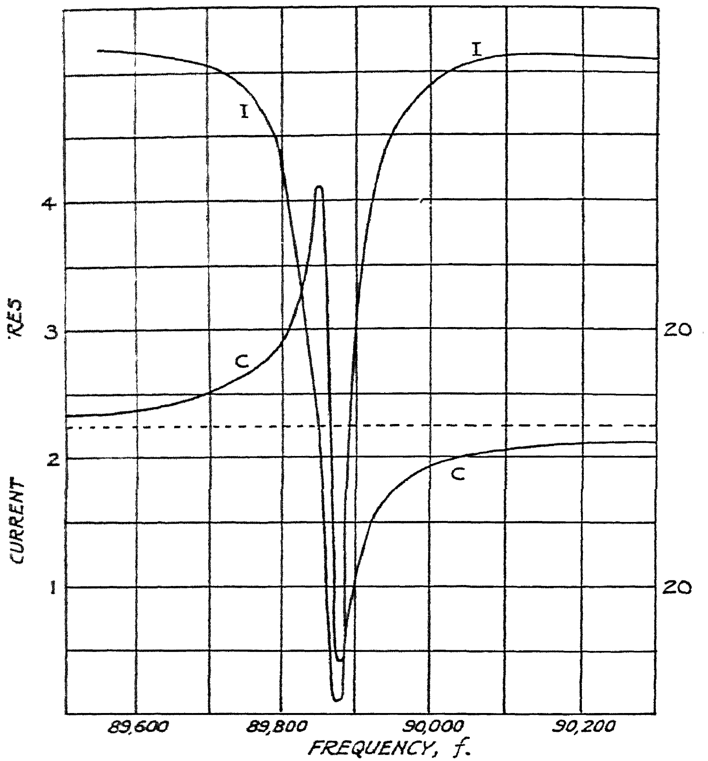


FIG. 15.—Characteristic curves of a piezo-electric resonator.

frequency is varied in the neighbourhood of resonance. As a typical example, a quartz resonator, approximately 30 × 4 × 1·4 mm., may be mentioned, which, when vibrating longitudinally (transverse effect) has a fundamental frequency of 89,870 cycles per second. When this resonant frequency is approached, the electrostatic capacity of the resonator, which normally is 4·5 micro-microfarads ($\mu\mu$fd), increases until at 89,860 cycles the equivalent parallel capacity is 42·2 $\mu\mu$fd. The capacity then decreases quickly to the normal value at resonance, passes through zero and becomes negative, reaching the value of —32·2 $\mu\mu$fd. at about 89,880 cycles per second. If the frequency is further increased, the capacity gradually returns to the normal value.

These variations in equivalent parallel capacity are represented in Fig. 15, in which the horizontal broken line indicates the "normal capacity" of the resonator. The diagram also shows the accompanying changes in I, the current in milliamperes in the oscillating circuit in which the resonator is connected, as the frequency is varied. As will be seen, the current descends to a very sharp minimum at resonance, this value being smaller the lower the resistance of the electric circuit. The equivalent parallel resistance of this resonator is practically infinite, except close to the resonant frequency, when it descends to a sharp minimum of about 20,000 ohms. The capacity reactance at resonance is approximately 400,000 ohms, so that, at resonance, this resonator functions practically as a pure resistance.

Pierce * was able, by a rearrangement of the electrical connections, to use the quartz so that it constituted an oscillator, capable of giving sustained oscillations with a constant frequency, determined solely by the frequency of the crystal.

4. Piezo-electric Resonators. Inasmuch as the resonator is itself a minute condenser, it is normally connected in parallel with the tuning capacity of a high-frequency circuit. This may be either the generator circuit, or a secondary circuit coupled thereto. The most suitable type of generator is the thermionic valve. The response when the generator is gradually tuned, until its frequency synchronises with a natural frequency of the resonator, may be detected either visually (ammeter, or galvanometer) or audibly (telephone receiver).

---

* *Loc. cit.*

The resonator may be used as a standard of high frequency, and thus a generator circuit that has been precisely adjusted to resonator frequency may be used to calibrate a wavemeter.

Dye * has developed the theory of the quartz resonator, using a theorem of Butterworth's,† in which the quartz system is replaced by an equivalent electrical circuit containing a capacity, C, inductance, L, and a resistance, R, all shunted by a capacity, C_1. In one particular case, where the quartz crystal was 7·0 × 0·6 × 0·15 cm., Dye found experimentally that $C = 0{\cdot}08\mu\mu$ farad, $R = 1{,}500$ ohms, $L = 160$ henries, and $C_1 = 8\ \mu\mu$ farad. On such a basis, almost perfect agreement exists between the forms of the current curve obtained theoretically and experimentally, respectively. The frequencies of the harmonics are, approximately, in the ratio 1 : 3 : 5 : 7, as would be anticipated from the simple theory.

Cady also used as resonators flat steel rods, excited by small plates of quartz, cemented to their sides at the middle. The plates were cemented to the steel with shellac, and the steel itself served as one coating for each plate, the other coatings being of tin foil, connected in parallel. Through the action of the transverse effect, the quartz plates expand and contract longitudinally, when connection is made to a source of electromotive force of the right frequency, causing a periodic condensation and rarefaction at the centre of the steel rod, whereby longitudinal vibrations are excited in the latter.

5. Piezo-electric Stabilisers and Oscillators. To a greater, or less, extent a resonator of any of the types described above will stabilise the frequency of the generator circuit to which it is connected. The crystal acts merely as a small additional capacity, except close to its own natural vibration frequency, when the effective capacity of the crystal changes with the frequency in such a manner as to tend to compensate for the variation in frequency. For good stabilisation the quartz plates should be considerably larger than is necessary for resonators, when used as frequency standards.

A quartz plate that stabilises well can, in general, be made to serve also as a piezo-electric oscillator. When properly connected to a valve, a sufficiently large fraction of the power which it receives from the valve, and which maintains it in vibration, is returned to the grid, to sustain the electric oscillations in the circuit, without any electrical tuning, or auxiliary feedback. Of the various possible modes of connection one, due to Pierce, is shown in Fig. 16. The piezo-electric crystal vibrator, B, has one of its electrodes connected to the grid, G, of a thermionic valve, and the other electrode connected to some point below the inductance (load) as, for example, the positive end of the battery. A micro-ammeter, A, and a telephone shunted by a by-pass condenser, C, are included in the plate circuit. The telephone, acting as a choke, and the bypass condenser are usually necessary to provide the proper reaction so that the system oscillates. This arrangement causes the crystal to vibrate with a period determined by the

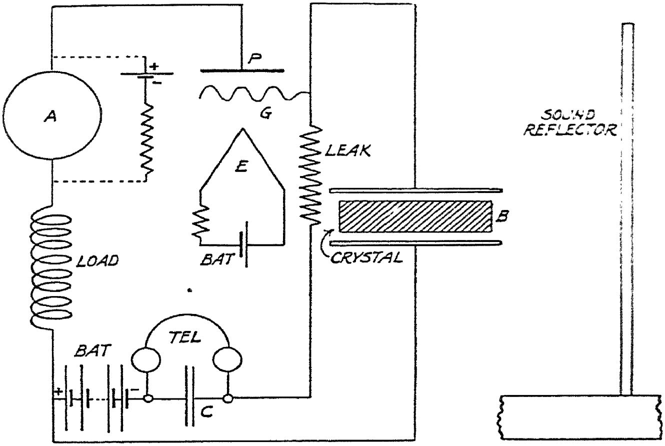


FIG. 16.—Generation of oscillations by means of a piezo-electric crystal.

mechanical frequency of the crystal slab, expanding and contracting along the direction of the B axis, so that vibration (sound) is radiated in this direction.

6. Ultra-sonic Waves. Pierce used this arrangement to explore stationary high-frequency, or ultra-sonic waves, as they are termed. The reflected sound wave from the reflector, falling on the emitting face of the crystal vibrator, even when the reflector in some cases was at a distance of 300 half-waves of sound from the vibrator, reacted on the crystal with sufficient force to cause the reading in the milliammeter A to fluctuate visibly, in accordance with the phase of the reflected waves.

The apparatus oscillates with a highly constant fixed frequency, determined by a mode of mechanical vibration of the crystal plate. It thus produces sound waves, and, at the same time, the strength of the plate current determines the relative phase of the direct and reflected sound waves in air. Thus the distance between successive loops of the stationary sound wave, for a range of 100, or more, half wave-lengths, may be measured with great precision, by merely varying the distance between the reflector and the radiating face of the crystal. This distance may be varied by means of a calibrated precision screw.

Pierce found that the velocity of sound in air varied with the frequency, and that at $f = 1{,}034{,}060$, carbon dioxide gas was practically opaque to sound. At $f = 98{,}183$, it was found that transmission through 17 mm. of this gas reduced the reflected intensity to the same extent as 68 mm. of air. Abello * observed that both carbon dioxide and nitrous oxide gases absorbed the ultra-sonic waves very highly. Helium absorbed less than hydrogen and ethylene appeared to have an absorption coefficient of the same magnitude as that of carbon dioxide and nitrous oxide. Pielemeier † has found that the velocity of these high-frequency waves in gases varies with the intensity of the sound, and Reid ‡ attempted to obtain the value of the velocity of sound at frequencies from 4×10^4 to $2{\cdot}16 \times 10^5$ cycles per second, under

---

. *Rev.*, 31, 1083 (1928).
34. 1184 (1929

conditions simulating outdoors. An apparent increase in wave-length was noted for regions close to the source, the increase at any given position being greater the lower the frequency. As the distance from the face of the oscillator increased, the velocities at various frequencies appeared to approach a common value. The values of the ratio of the specific heats of air, deduced from the velocity at 14 × 10^4 cycles per second, was 1·4035, which is in good agreement with the value computed from the velocity of sound at audible frequencies. The change in the velocity of sound, caused by saturation with water vapour, was found to be 1·37 metres per second.

Thompson,* using a crystal vibrating at 108,600 cycles per second, measured the velocity of sound in water vapour. At a temperature of 27° C. the velocity was found to be 432 metres per second. This value agrees fairly well with that of Neyreneuf,† *viz.*, 431 metres per second.

Hubbard and Loomis ‡ employed the ultra-sonic interferometer method to study the velocity of sound in various liquids. The apparatus consisted of a cylindrical chamber, containing the liquid to be studied, in which plane compressional waves were produced by the piezo-electric crystal plate. The waves were reflected by a movable piston, which could be displaced by means of a micrometer screw, so as to be set at successive positions for the production of stationary waves. The frequency of the oscillation was so high that the wave-length in the liquid was short in comparison with the diameter of the plate. Under these conditions, the effect of the walls of the vessel may be entirely neglected, provided that the piston is within a few centimetres of the plate. The method is thus free from the troublesome corrections that have hitherto been necessary when measuring the velocity of sound in tubes by resonance. Sound-velocities have been determined at different temperatures, in water, mercury, and in a number of solutions of sodium chloride, potassium chloride, and sodium iodide. The thermodynamic coefficients for water and mercury,

* *Phys. Rev.*, **36, 77 (1930).**

† *Ann. d. Chim. et d. Phys.*, **9, 535 (1886).**

‡ *Phil. Mag.*, **5, 1177 (1928).**

ed from the results, agree with those obtained from the ridgman.

Theory and calculation predict that no sensible diminution of the velocity of high-frequency waves in a liquid is to be expected, unless the viscosity of the liquid is very great, and the frequency very high. Boyle and Taylor[†] have shown that between the frequencies of 43,000 and 600,000 per second in water, the diminution is only 5 per cent. Further experiments[‡] with water and castor oil, using a stationary wave method, gave velocities in these liquids of $1{\cdot}48 \times 10^5$ cm. per second at 18·5° C. and $1{\cdot}43 \times 10^5$ cm. per second at 20° C., respectively. The velocity of sound in a liquid is, therefore, independent of the frequency, although it varies, *e.g.*, in sea-water, with pressure, temperature and salinity.

An ultra-sonic beam has been used by Langevin[§] and Boyle and Reid in the detection of icebergs and in depth-sounding. As a result of tests on shores and reefs, it was considered ordinarily possible to obtain ranges (for definite echo reception) up to about 1,000 yards. With regard to icebergs, the conclusion was drawn that they can be detected, by an ultra-sonic beam, over a short range (200 to 300 yards) in deep water, but that the reflected beam is weak in comparison with that from steel ships, or rocky shores. With regard to depth-sounding, the ultra-sonic apparatus gave clear, strong and sharply defined echoes from the sea-bed. It was found that the ultra-sonic method of sounding was practicable at all depths, over a few fathoms, the speed of the ship making no difference to the observations. In all these cases, the ultra-sonic transmitter also acts as the receiver of the echo.

These high-frequency sound waves also show other remarkable effects. For example, projected against the free surface of oil, they cause a mound to appear on the oil surface. If passed across the boundary surface separating two liquids, more or less stable emulsions are formed. Chemical reactions are accelerated and

---

[*] See Section 1, Chapter III.

[†] *Roy Soc. Canada. Trans.*, 19, 197 (1925).

[‡] *Ibid.*, 21, 79 (1927).

[§] French Patent, No. 505, 903 (1918).

[‖] *Roy. Soc. Canada Trans.*, 20, 233 (1926).

crystallisations started. At frequencies from 300 to 400 kilocycles per second, the heating of liquids by these waves is very pronounced. The waves also have great effects upon living matter. Red blood corpuscles in physiological salt solution are rapidly destroyed, the turbid liquid becoming as clear as a solution of red aniline dye. Small fish and frogs are killed by an exposure of one or two minutes.

7. The Intensity of Sound. Many instruments have been devised to measure the intensity of sound, but in several cases it is necessary to make certain assumptions, often unjustifiable, to convert their indications into absolute measure. All known measuring devices are limited to certain ranges of frequency and intensity; they are best suited to a particular medium through which the sound waves pass, and their indications are dependent on the dimensions relative to the wave-length of the incident sound. In some cases it is assumed that the pressure fluctuation at the surface of the sound receiver, which is to measure the intensity, is the same as that which would occur in the undisturbed sound wave. Sometimes the other extreme view is taken that the pressure is doubled by reflection. In practice, neither of these assumptions is correct, but it is possible to define experimental conditions so that the results agree, approximately, with one of them.

Absolute sound intensity measurements are difficult, although not impossible, but comparative sound-intensity measurements are possible with almost all forms of sound receiver. The refined condenser microphone is used for feeble sounds, its action depending upon the variation of the electrical capacity, caused by air pressures deflecting one plate of the condenser. It is used with a valve amplifier. Other methods include the sound-pressure radiometer, the hot-wire microphone * (with, or without, resonator), and interferometer methods of observation of the variation of refractive index.

At a frequency of 2,000 per second the minimum audible sound corresponds with a pressure of 6×10^{-4} dynes per sq. cm., and an amplitude of 2×10^{-9} cm.; while pressures up to 6,000 dynes per sq. cm., and amplitudes up to $1{\cdot}7 \times 10^{-4}$ cm., are still recognisable as sound.

---

* See Section 2.

Changes of intensity of a *monotone* cannot be perceived under most favourable conditions unless they exceed 10 per cent. of the original, and thus the total audible range of intensity can be traversed in about 270 barely perceptible steps. It has been suggested that, with distinctly perceptible differences of intensity, 120 equal percentage-steps may be arbitrarily assumed to cover the range from the faintest to the loudest sounds. Hence 120 degrees of a sensation-scale have been adopted by some workers as corresponding to the whole range of the ear; and consequently, if one sound contains x times the energy of another, the sensation ratio is $10 \log_{10}x$ degrees.

Now the sensation of sound may be measured either by the energy flow that causes the sensation or, alternatively, by the strength of the sensation. The measurement of this strength is really a psychological problem, and the main suppositions in attempting such measurement are that changes of sensation can be compared with some accuracy, and that our perceptions of such changes are related to the energy changes by the rule that equal steps of sensation correspond with equal percentage rises of the power causing the sensation. In other words, the logarithms of the steps in power may be used as the measure of steps in the corresponding sensations.

Now, if an observer aurally compares two equal telephones, one at the input-end and the other at the output end of a mile of standard cable, the frequency being 800 cycles, he observes a change in the sound intensity which is called the 800 cycle standard-mile. The difference in strength is due to electrical dissipation in the cable. The amount of this change, or this step in sensation as we might term it, corresponds, approximately, to a step of 25 per cent. in power. Hence has arisen a proposal to standardise a power step of ratio $10^{0{\cdot}1}$ (which is equal to 1·259) and to generalise it so as to apply it to express the ratio of two powers of any nature and any frequency. The corresponding standard step in sensation is called a *transmission unit*. It can be calculated from any given set of measurements by taking the logarithm of the power ratio to the base 1·259, or, what is the same thing, taking the logarithm of the power ratio to the base ten and multiplying by ten. We have therefore the following relations between the ratio of the powers causing sound sensations and the number of standard steps of sensation by which the sensations differ.

Power ratio . . .	1·259	2	4	10	100	1,000
Steps in sound sensation or "transmission units" . . .	1	3	6	10	20	30

The other important subject-matter in psychological acoustics, the sensation of pitch, also proceeds by ratios, and, further, the makers of keyboard instruments have adopted, without knowing anything of logarithms, a logarithmic scale for their instruments—equal distances along the keyboard represent equal ratios in pitch. Hence we conclude that the most human way of representing acoustical response relations graphically is to use transmission units for intensity as one co-ordinate, and logarithms of frequencies as the other co-ordinate.

In the acoustics of the ear, Wegel and Lane[*] have shown qualitatively, and quantitatively, that no sound, even when very intense, can diminish, or obliterate, the sensation of a concurrent sound which is lower in pitch. Low tones are easily masked, if not much lower than the masking tone (except in so far as beats may enter), but are not easily masked if much lower than the masking tone ; and high tones can be masked by low tones when the ratio of the intensity of the latter to the former reaches a definite value. Wegel and Lane have separated the type of masking which occurs in the ears from that which occurs in the brain. The same investigators have applied their methods to the successful unravelling of old problems concerning combination tones, arising from the non-linear response of the ear.

Michelson's interferometer principle has been used to measure small vibrations ; for example, Thomas and Warren[†] utilised it to measure the vibrations encountered in telephone diaphragms and structures. The essential principle of operation is that in which one plate is attached to the vibrating system and the other plate is fixed. The fringe system is observed as the current in the telephone is increased from zero. When the vibration of the diaphragm is very small, the fringes are blurred and disappear, but as the amplitude of the vibrating plate is increased, they reappear, becoming distinct when the peak value of the vibration is $\lambda/4$, where λ is the wave-length of the light employed. The fringes, however, will be displaced by half a fringe width from the original fringe system, when the diaphragm was stationary. They reappear in this manner every time the peak value of the vibration is a multiple of $\frac{\lambda}{4}$, alternately in their original and displaced positions. The method can be adapted readily for the study of the vibration of light moving systems.

---

[*] *Phys. Rev.*, 23, 266 (1924).

[†] *Phil. Mag.*, 5, 1125 (1928).

8. Architectural Acoustics. Our scientific knowledge of the acoustic properties of closed rooms is due almost entirely to the work of Sabine,* who argued that a sound, created in a closed room, is ultimately distributed by repeated irregular reflections so that (leaving foci out of account) each cubic centimetre of air is traversed by waves proceeding in every direction. He stated that sound can only decay by absorption in the walls and furniture, and he showed that, in general, there are several hundred reflections before the echoes disappear. It has long been known that when the decay is unduly slow, the acoustics of a room are defective, and the defect is now called *reverberation*. Sabine introduced the idea of measuring the reverberation time of a room, defining the duration of reverberation as the time taken for a sound of a million times that of bare audibility to die down to its threshold value. This definition was given, and Sabine made measurements of the reverberation times of rooms before modern electrical methods came to the aid of acoustics, but the subject attracted little attention. Since the arrival of the amplifier, however, the subject has sprung to life in every country.

---

* "Collected Papers on Acoustics," 1922, *Acoustical Soc. of America* . 2, 434 (1931); see also Békésy, *Ann. d. Phys.*, 8, 851 (1931).

The three propositions which contain the gist of the theory of reverberation are :—

(i.) The duration of audibility of the residual sound is nearly the same in all parts of an auditorium.

(ii.) The duration of audibility is nearly independent of the position of the source.

(iii.) The efficiency of an absorbent in reducing the duration of the residual sound is, under ordinary circumstances, nearly independent of its position.

Sabine also postulated three simple rules to be followed, if satisfactory results are to be obtained in a room :—

(*a*) The sound must be sufficiently loud.

(*b*) The quality of the sound must be unaltered. *i.e.*, the relative intensities of the components of a complex sound must be conserved.

(*c*) The successive sounds of speech, or music, must not overlap, but must remain distinct.

From a scientific point of view the design of an auditorium, which is acoustically perfect, involves three principal factors—resonance, interference and reverberation. The reverberation time of a room is defined above as the duration of audibility of a sound which had initially the intensity 10^6 times the minimum audible intensity. Denoting this time by t, it has been shown * that :—

$$t = \frac{53{\cdot}5\ V}{av}$$

where V is the volume of the room, a, the *absorbing power* of the whole room, and v, the velocity of sound at the temperature of the air in the room ; a is defined by the equation $a = \alpha S$, where α is the average absorptivity of the interior exposed surface, and S, the internal exposed area of the room and its contents.

The commonest acoustic defect of modern, hard surfaced, lecture-rooms and auditoriums is the overlapping and confusion of successive sounds, such as the syllables of a sentence, by too great reverberation. The above equation shows that the remedy is to increase the absorbing power of the room, and it also permits of computing the reverberation time in advance of construction, from the known absorptivities of the materials of which the exposed internal surface is to consist.

---

* See Buckingham, " Bureau of Standards, Science Papers," No. 506 (1925) ; Watson, " Acoustics of Buildings " (1922).

An important factor, and one that must be known when correcting, or designing, the acoustics of an auditorium, is the time of reverberation that will give the best results. Sabine prescribed 2·31 seconds as the acceptable time of reverberation for the Boston Music Hall of 649,000 cubic feet. In another case, involving a number of small music studios in the New England Conservatory of Music, of which the volume varied from 74 to 210 cubic metres (4,276 cubic feet for the average of five rooms), a number of musical experts listened in each of these rooms to piano music, as increasing amounts of absorbing material were introduced, and expressed opinions concerning the acceptable condition for the best effect. On the basis of these opinions Sabine conducted subsequent experiments, and calculated the average time of reverberation to be 1·08 seconds as the suitable time for rooms of this size. In general, for speech and light music, the optimum time is about 1·0 sec., and for orchestral, or grand music, about 2·5 sec.

The absorbing power of the whole room is given by the equation :

$$a = \frac{4V}{\quad}\log \quad E_1 \qquad 1$$

where E_1 and E_2 are the values of the intensity of the sound source, and t_1 and t_2 are the corresponding times of duration of audibility of the residual sound. E_1/E_2 will be known from the arbitrarily chosen ratio of the powers of the two sources ; and only the two durations of audibility, t_1 and t_2, have to be determined experimentally.

The sound absorption by specimens of material only one or two square feet in area may be measured by means of a stationary wave method. The specimen is fixed with the aid of a suitable holder at one end of a pipe, and a constant source of sound placed opposite the other end of the pipe. The whole (source and pipe) may be enclosed in a sound-chamber. The presence of the absorptive material results in stationary waves being formed in the pipe, for which the amplitude at the "loops" reaches a minimum instead of zero value. The coefficient of absorption is given in terms of the ratio of the pressure amplitudes at the maxima and minima, respectively. Paris * has measured these pressure amplitudes by means of a special hot-wire microphone, tuned to the frequency of the source, certain errors being eliminated by a method of comparison with the waves in the same pipe, when a practically perfect reflector replaces the absorbent. The source of sound was an oscillator and loud speaker. Results are given, chiefly for a frequency of 512, but in some cases also for frequencies of 380 and 650, for a number of materials, chiefly acoustic tiles and experimental acoustic plasters. A large effect was noted with one particular plaster when the thickness was altered.

Tables of coefficients of absorption, obtained by various methods, are given by Davis and Kaye.† The values vary according to the porosity of the material, *e.g.*, 0·01 for various hard substances, such as metal, glass, wood, *etc.* ; 0·5 for thick carpets, audiences, acoustic tiles and plasters, 1·0 for an open window.

A good anti-reverberation material should reflect as little as possible and absorb a maximum of the incident energy of the sound. The first condition implies that the acoustic resistance of the absorbing material should be as nearly as possible equal to that of the incident medium, and the second condition requires that the damping must be a maximum, so that the transmitted sound is suppressed in a very thin layer of the material.

With the introduction of the valve amplifier, accuracy has been introduced into the prescription of the best reverberation value for speech, for singing, for instrumental music, respectively, and in halls of various sizes. The acoustic data of some of the principal concert-halls and debating chambers of the world have been determined and published; empirical laws connecting the optimum reverberation values with the volume of these halls have been established, and the absorption of objects placed in rooms has been determined by methods based on Sabine's definition of reverberation. As a consequence, it is now possible to measure the defects of a given auditorium and to calculate, with fair certainty, the amount of absorbing material that should be permanently introduced to correct these defects. In addition, it is now easy to plan buildings, before their erection, to have a desired reverberation time—in fact, to be of good acoustic quality.

---

* *Phys. Soc. Proc.*, **39**, 269 (1927).

† "Acoustics of Buildi--- "

The advances in our knowledge of the acoustics of buildings have led to, or aided, many noteworthy practical applications. The most important of these is possibly that of magnifying the voice of an orator, so that it may be audible to large audiences. In rooms and halls the problems of echoes and foci, of resonances and reverberation, all tend to be exaggerated by the magnified intensity of the sounds; and electrical vibration of the apparatus, caused by waves from the loud speaker reaching the microphone (in addition to the original waves), easily leads either to singing, or to distortion. The most frequent type of distortion has proved to be that caused by the unequal treatment of sounds of different frequencies, in either the microphone, the amplifier, or the loud speaker: but in the study of these public address mechanisms still other types of distortion, originally unsuspected, have appeared. One of these arises from the fact that when a sound is started, or stopped, a transient vibration of the chain of apparatus, or of the auditorium, may be excited, and this adds itself to the original sound; another trouble may arise from the asymmetric treatment, in any portion of the apparatus but especially in the amplifier, of pure sounds—this introduces sum and difference tones which may cause dissonances in music, or unintelligibility in speech. Inasmuch as it is usually found necessary to amplify the wanted sounds until they are ten thousand times as intense as the unwanted disturbing sounds, arising from a big audience, the distortions, dissonances and transients just mentioned have placed many difficulties in the path of the development of these appliances for assisting orators. Fortunately, the ear is so bad a judge of intensity of sound, that exact equality in the magnification of each of the frequencies in a complex sound is not required. In fact, certain frequencies of the speech range may be magnified in intensity ten times as much as certain other frequencies in that range, without the ear noticing the inequality of amplification; and certain frequencies may be altogether omitted by the apparatus from the reproduction of a speaker's voice, without loss of intelligibility and naturalness. It has been found better to divide the amplified speech currents among a number of well-distributed loud speakers than to deliver it all to one powerful loud speaker; for it is a curious fact that when the intensity of a complicated sound—either speech, or orchestral music—is greatly magnified, perfectly equally at every frequency—that is to say without any distortion whatever—and delivered to the ear, the listener believes that the sound is badly distorted, partly as a consequence of the non-linearity of the mechanism of the ear.

Speech sounds, ranging from 100 to 6,000 in frequency, can be magnified fairly equably; and most of the spectrum of the consonants, *f*, *s*, *th*, between 4,000 and 10,000 in frequency, can be reproduced. The intensities of the sounds to be dealt with vary in the ratio 1,500 to 1 in the case of speech, and in the ratio 100,000 to 1 in the case of music.

9. Sound Ranging. If we know the velocity of propagation of sound, the unknown distance, d, between two points may be determined by measuring the time interval, t, that the sound takes to travel from one point to the other, *i.e.*, $d = vt$, where v is the velocity of sound. This method may be modified by reflecting the sound after it has passed an observation station, so that after an interval, $t = 2d/v$, it returns again to the station. A third method consists in sending out at the same moment two sets of waves which may, or may not, be of the same type, the two sets of waves travelling through different media. An observer at a distance d from the source of the waves observes the time interval between the reception of the two types of waves, and from the relation :—

$$t = \frac{d}{v_2} - \frac{d}{v_1},$$

where v_2 and v_1 are the velocities of the two sets of waves, the value of d may be determined. One set of waves may be light, or wireless waves, travelling with a velocity of 3×10^8 metres per second, compared with the velocity of sound, of the order 3×10^2 metres per second in air, or $1{\cdot}5 \times 10^3$ metres per second in water. The two sets of waves may also be of the same nature, *e.g.*, sound waves, simultaneously propagated through water and the air.

Echo-ranging. The reflection method of determining distance is often referred to as the *echo method*, and has been extensively used to determine depths at sea. Until comparatively recently the simple method of the " lead " was employed without modification, but subsequent to the development of the hydrophone, methods based on the reception of an acoustic echo from the sea-bed have been devised in the United States, France, Germany and Great Britain. In all these methods a sound source transmits acoustic vibrations through the water, and the reflected sound from the sea-bed is received by means of a hydrophone. The methods differ in the means of determining the depth.

In the German method the depth is estimated by measuring the intensity of the echo. A source of sound on one side of the ship emits continuous waves which, reflected from the bottom of the sea, are received by a resonant chamber which causes a tuning fork to vibrate. The intensity of the reflected sound is measured by the amplitude of the fork, as observed by means of a microscope. Obviously this will be unsatisfactory in practice, for sea-bottoms of mud, or of rock, will have different coefficients of reflection. In another method the source sound is an electrically-fired detonator, which gives a single impulse to the water. The impulse reflected from the bottom is received on the opposite side of the ship. At the instant of firing the detonator, an electromagnetic device releases a disc, which commences to rotate. The rotation is suddenly arrested when the echo reaches the receiver, the edge of the disc being graduated to indicate depths directly. This apparatus, which gives reliable soundings up to 80 fathoms, has also been used on airships as a means of determining their height above the ground.

One American system, invented by Fessenden, is illustrated in

Fig. 17. A disc, A, made of insulating material, is rotated at a uniform speed by means of a motor, B. The disc carries a conducting segment, C, that closes the electrical circuit through a sound transmitter, D, when it passes beneath brushes, E, thereby sending out a sound signal. This segment also closes the circuit through a telephone receiver, F, when it passes across the brushes, G. If the echo of the signal meets the microphone, or other type of sound receiver, H, at the instant segment C short-circuits brushes G, it will be heard in the telephone receiver, F, and the time of sound transit from the transmitter to the receiver, by way of reflection from the sea-bottom, will be equal to the time required for segment C to travel the angular distance subtended between the two pairs of brushes, and indicated by the pointer, K, on the scale, L. This condition is brought about by rotating brushes, G, about the insulating disc, A, by means of the handle, M. In practice, the disc must be rotated at considerable speed, or the angle swept out by the segment, while the sound travels to the sea-bottom and back, will be too small to measure with sufficient accuracy. This results in sending out sound signals in rapid succession and the return of echoes from the sea-bottom in still more rapid succession, for the reason that a sound signal

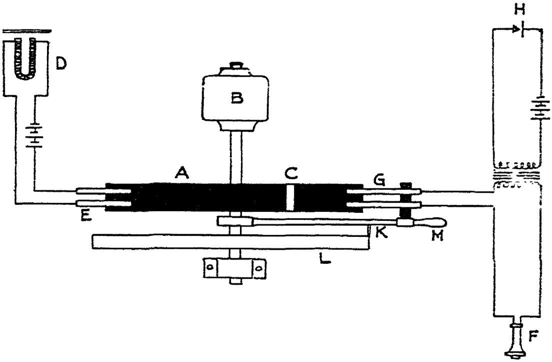


Fig. 17.—The Fessenden sound-ranging apparatus.

usually echoes back and forth between the surface and the sea-bottom several times before its energy is absorbed. Under such conditions sound can be heard in the telephone for numerous settings of the brushes, G, and the relation between the depth and the scale reading becomes indefinite.

In the *reflection method,* used by America, the propeller of a vessel represents the source of sound, and two receivers are spaced at a distance apart on a horizontal line passing through the propeller. The sound will be reflected from the sea-bottom, and there will be a difference in the time of arrival at the two receivers. The sound is made to reach each of the observer's ears at the same time by altering the energy conducting path, leading from each receiver to its respective ear; the difference in times of transit from the receiver to the ear is thus determined, and is equal to the difference in time of arrival at the two receivers.* If $2d$ is the distance separating the source and the receivers, and the sound waves make an angle, ϕ, with the horizontal sea-bottom, the depth, h, of water below the propeller is given by, $h = d \tan \phi$. This method becomes inaccurate when the slope of the sea-bottom varies from the horizontal. In this case a sound transmitter and receiver are installed at each end of the vessel, one operator working the first transmitter and the second receiver, and then the second transmitter and the first receiver. Thus the slope of the sea-bottom can be determined. This reflection method is suitable for measuring depths less than about 100 fathoms.

The *stationary wave method* is also used in the United States. The sound transmitter is driven by means of an alternating current, so designed that the frequency of the current can be controlled, and varied, by the operator over the range included between about 500 and 1,500 cycles per second. This circuit is provided with means for indicating the frequency with a high degree of accuracy at all times. The operator uses a two-telephone head set, one phone of which is inductively connected with the alternating current circuit that drives the sound transmitter. The other phone is connected with the input from the sound receiver, which is situated at the same horizontal level as the transmitter, and at a known distance from the latter. With the phones connected in this way, the sound heard in the inductively-connected phone has, at all times, a definite phase relation with the sound waves leaving the transmitter, and the sound generated by the other phone has a definite phase relation with the sound waves reaching the receiver. If the operator adjusts the frequency properly, he can make the sound heard in the two phones have the same phase, and can recognise this condition through the fact that the sound will then be binaurally centred. If the sound waves leaving the transmitter have the same phase as those arriving at the receiver, then the sound path between transmitter and receiver, *viâ* the sea-bottom, represents a whole number of wave-lengths. If this path length is S, and N is the number of wave-lengths in the stationary wave system,

---

* This arrangement, whereby an artificially increased path-length is introduced in the side which is nearer the sound source, is called a *binaural*

$$S \qquad Nv$$

where n is the frequency of the sound.

Suppose the operator adjusts the frequency so that the sound is binaurally centred. Let the frequency be n_1; this will be equal to the frequency of the alternating current. Then suppose he slowly raises, or lowers, the frequency. He will notice that the sound apparently passes away from the binaural centre. and finally comes back across centre. Each time the sound comes back across binaural centre, he has varied the number of waves in the stationary wave system by one. Suppose he varies the frequency until the number of waves in the system differs from the number in the original system by a, and he determines this number by counting the number of times the sound comes to a binaural centre, while he slowly changes the frequency. If the final frequency is n_2, we have :

$$: \frac{Nv}{n_1} \qquad \qquad \frac{v}{n_2},$$

and
$$S = av$$

which gives a very simple working formula for determining S, the sound path from the transmitter to the receiver, *viâ* the sea-bottom. This method has proved to be extremely accurate for measuring shallow depths. It gives greater accuracy as the depth becomes more shallow, for the reason that the less the depth, the greater the change of frequency that is required to change the number of waves in the system. The method breaks down at great depths for the reason that a small change in the frequency introduces so many waves into the system, and so rapidly, that they cannot be accurately counted, and thus the factor a becomes indefinite.

In the French system a detonator is fired near the ship, and the time interval measured between the instant of firing and the arrival of the echo. The apparatus has been made automatic and self-indicating, but has the disadvantage that a large supply of detonators is required to take a line of soundings over a considerable distance. In another method high-frequency vibrations of a quartz crystal are employed, and by means of steel discs the frequency of the crystal is adjusted to a suitable value, *e.g.*, 50,000 cycles per second. An alternating electromotive force from an oscillating circuit is applied to the discs, and tuned to the resonance frequency of the quartz-steel oscillator. A pulse of high-frequency waves is emitted from this transmitter, and after reflection, falls upon the quartz oscillator again, a switch in the meantime connecting the oscillator to the receiver. The emission, or reception, of the pulse is indicated by means of a spot of light from an oscillograph on a scale, graduated in fathoms, or metres. The spot of light is made to move uniformly along the scale, and by means of switches it is arranged that the impulse starts from the oscillator when the spot is passing through the zero position. The reception of the reflected impulse is indicated by a slight deflection of the spot, which in the interval has moved along the scale. Knowing the velocity of sound in water, and the rate of motion of the spot of light, the equivalent distance in fathoms, or metres, corresponding to the observed distance moved by the spot of light, is known. If required, signals may be transmitted once per second and a continuous record of the depth obtained. This system has been applied not only to depth measurements but also to the location of shipwrecks and icebergs.* Small projections, such as wrecks, may be missed by ordinary echo-sounding apparatus, which tends to give an average depth over an area, rather than the absolute depth at a point directly below the ship. For navigational purposes it is, of course, important to have warning in advance of an obstruction. This the apparatus employing audible sounds does automatically, while high-frequency apparatus, such as the Langevin arrangement, only gives the distance of an obstacle which is more, or less, in line with the beam.

The British system utilises a sonic, or audible-frequency source of sound, a steel diaphragm, fixed to the hull of the ship, and this is set in vibration by a small spring hammer which is withdrawn at regular intervals from the diaphragm by means of a solenoid. A simple microphone, enclosed in a carefully designed rubber body and compartment, forms the receiving hydrophone. A 1/8th horse-power motor, running at 1,800 revolutions per minute, drives two switches through a 10 to 1 reduction gear. These switches consist of brushes, bearing on a rotating disc with insulated segments. One of them breaks the circuit to the solenoid of the transmitter three times a second for about 0·0025 second, whilst the other, running on the same shaft, short circuits the telephone in the receiving circuit, except as determined by the position, relative to the corresponding pair of brushes, of a second insulating segment. This latter pair of brushes can be displaced by a hand wheel, and if a sound is heard in the telephone, we know that the time taken for the insulated segment of the disc to travel the amount of the displacement must be the same as that taken by the transmitted sound to travel to the bottom of the sea and back to the receiver. The velocity of sound in water and the revolution rate of the switches being known, it is possible to graduate this displacement of the brushes in terms of the depth in fathoms. This is done on a circular scale on the hand wheel. It is clear that the speed of the motor is all-important, and a specially designed centrifugal governor controls it to a constancy of 1 per cent., despite variations in the supply voltage. The Admiralty pattern echo-sounding apparatus for *shallow* water measurements is shown in Fig. 18. Another type, called the *oceanic*, is suitable for depths from 30 to 4,500 fathoms. Similar principles underlie both types, but one of the main differences of the oceanic type, from that described above, lies in the transmitter which, instead of employing a spring-loaded hammer, is actuated by a pneumatic one.

---

* See International Hydrographic Bureau, Special Publications on "Echo-Sounding," No. 3 (1924) and No. 4 (1926).

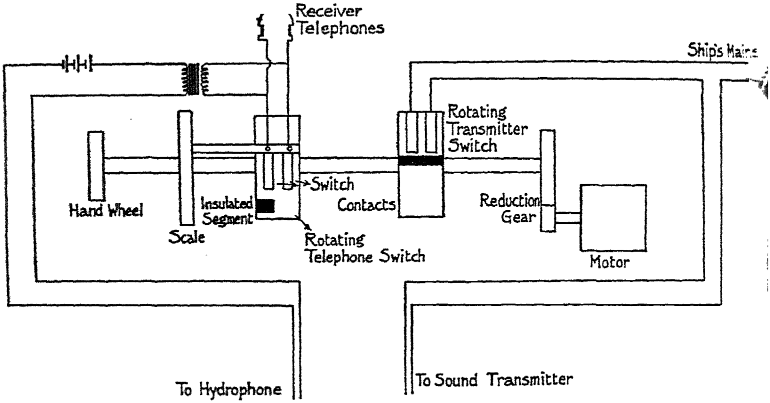


FIG. 18.—The British echo-sounding apparatus.

One difficulty is the response by the receiver to the waves emitted directly from the transmitter, besides those echoed from the bottom of the sea. Owing to the small time interval which elapses before the echo returns in shallow water, the receiver must be able to recover very rapidly, and to effect this, the transmitter must not be one that sends out waves of considerable duration in time. With the impulse from the small hammer, it has been found possible to measure the depth of water when it is only just enough to float the ship.

Another method of damping the impulses that are transmitted by the water directly to the receiver, is by the suitable placing of the latter with reference to the transmitter. Were they to be mounted close to one another in the bottom of the ship, the amount of energy absorbed by the receiver would, in shallow water, render it insensitive to the returning echo.

Radio-Acoustic Method. The methods described above for determining the range, or direction, of a source of sound utilise a continuous, or frequently repeated, sound. Other methods must be devised for locating sources of sound, such as gun-firing, or a charge exploding. In addition to those used in the late war, another method has been developed by Wood and Browne * known as the radio-acoustic method. Its underlying principle is briefly as follows: The ship to be located emits a simultaneous wireless signal in air and an explosion wave in water. The distances measured in such a case are solely dependent on a knowledge of the time interval between the reception of the two waves and the velocity of propagation of the explosion wave in water, for the time of propagation of the wireless wave is negligible, by comparison. The apparatus consists of :—

(*a*) A means of producing the wireless signal at the instant of explosion of the charge.

(*b*) Two, or more, acoustic receivers under water—the positions being accurately known—and a wireless receiving set at the recording station.

(*c*) A means of recording, and timing, the radio-acoustic signals.

A double key can be used, one part of the key firing an electrical detonator in the charge, the other part transmitting the wireless signal. If greater accuracy is required, an automatic arrangement can be employed, whereby the shock of the explosion automatically closes a circuit and transmits the wireless signal.

In the experiments, four hydrophones were used, laid on a line approximately north and south, just eastward of the Goodwin Sands. Each hydrophone was connected to a string of an Einthoven galvanometer, another string recorded the half second ticks of a Greenwich chronometer, and a sixth string recorded the reception of the wireless signal. From the records can be deduced (1) the total time interval from the charge to each hydrophone, (2) the time of passage of the explosion wave between each pair of hydrophones. If t_1, t_2, t_3, *etc.*, represent the various time intervals between the instant of firing and the arrival of the explosion wave through the water, the distances of the explosion from the various hydrophones are vt_1, vt_2, *etc.*, where v is the velocity of sound in water, supposed known. As the positions of the hydrophones are known, the intersection of circles of radii vt_1, vt_2, *etc.*, locate the position of the explosion.

---

* *Proc. Phys. Soc.*, **35, 183 (1923).**

Charges were fired at various points around the Goodwin Sands. In no case, when a charge was fired to the westward of the sands (the hydrophones lying to the eastward) was any effect recorded, the explosion wave failing to penetrate the sands, or to pass over the shallow water (3 or 4 feet) covering them. Firing charges in other positions, only partially screened by the sandbank, indicated that the latter was casting a very efficient acoustic shadow. In one experiment some evidence of distortion at the edge of the sandbank was obtained, the record suggesting that an acoustic wave (of long wave-length) resulting from the explosion, was either diffracted round the edge of the sandbank, or that the main pressure wave was retarded in velocity, and changed in wave form, as it passed over the shallows at the edge of the bank.

These experiments indicate the possibilities of the radio-acoustic method when applied to the navigation of ships. It was possible to give a vessel an accurate position within ten minutes of receiving her request for a location. The method has also been used successfully in fixing accurately the positions of certain buoys and light vessels out of sight of land. The Geodetic Survey of the United States is at present using a modified form of the method in surveying coastline and banks, and in locating marked buoys. Wood and Ford * devised an instrument, known as the phonic chronometer, which is alternative to the Einthoven-recorder system of measuring time-intervals. This instrument is a type of stop-watch, operated electromagnetically, and fitted with three sets of dials for measuring independent time-intervals.

---

* *Journ. Sci. Inst.*, 1, 161 (1924).

The speed of the chronometer is governed by a tuning fork and a phonic motor giving an accuracy of 1 in 10,000. Time intervals are indicated directly on the dials to 0·001 second. Special explosion shock receivers were used with the chronometer, and the wireless signal started all the dials. They were stopped in turn as the explosion wave passed the respective receivers, and the time intervals were indicated directly on the dials.

10. Electro-acoustics. Many advances in acoustics have been made recently by introducing electrical ideas into the theoretical aspect of the subject. This interchange, as it were, is possible because vibration phenomena of all kinds approximately satisfy the same linear differential equations. Many acoustical problems can be translated into problems concerning electrical networks, and as there exists a great body of knowledge of such networks, the problem is often solved in the act of translation. In addition, where some new conception occurs in electrical vibration theory the analogy in sound can be sought. For example, van der Pol * has explained the flashing of a neon tube in a resistance-capacity circuit as due to what he terms a *relaxation oscillation*. Translated into mechanical phenomena, a relaxation oscillation is the communication of the vibrations of any mechanical system to a greater, or less, degree to other systems in contact with it. This explains certain acoustical phenomena, such as the squeaking of a slate pencil when it is rubbed on a slate. It also follows that the frequency of an accurate electrically-maintained tuning fork may be seriously affected by the manner in which it is supported.

Electrical ideas began to enter acoustics explicitly when the telephone receiver came to be investigated scientifically. The mathematical aspects of this investigation are very similar to those of the vibration galvanometer, and other various types of electrical machinery, such as the synchronous motor. In all cases we have a winding carrying alternating current, a magnetic field acting mechanically on the winding, and relative motion between the two. When the rotor of a motor, or the diaphragm of a telephone, is maintained in steady motion by the electro-dynamic forces due to the alternating current, the motion induces an electromotive force, which is proportional to the velocity and may, therefore, be regarded as due to a special impedance in the windings. Thus in the case of the telephone, the inertia, the elastic quality and the energy-dissipating property of the diaphragm can, at any given frequency, be represented quantitatively by a hypothetical reactance and resistance, provided the mechancial and electrical units are properly co-ordinated.

---

* *Phil. Mag.*, **2**, 978 (1926).

Webster [*] first emphasised the use of the conception of acoustic impedance for replacing, by a single complex number, all the quantities involved in the reaction of an acoustical system. From the formulæ for the typical impedances [†] most frequently met with in pure acoustics, namely, those due to inertia, elasticity and the production of free waves, he obtained general expressions for the impedance of the open end of cylindrical and tapering tubes. As a consequence, mainly of his work, our knowledge of horns has been much clarified. At the narrow end of a horn the energy enters in the form of plane waves, and so the source works at maximum efficiency ; at the open end the reactance due to inertia is minimised, and the rate of working of the atmosphere increased, by the largeness of the area. Consequently, the amount of sound emitted is increased, the waves are little reflected at the open end, especially if their length is small compared with the diameter, and standing waves, or resonances, are minimised.

What happens to sound waves passing between the narrow end and the open end of a horn depends upon the form of the tubular surface. This has been thoroughly worked out by the methods of Webster, and it is known that the exponential horn, that is, the horn of which the sectional area increases by equal percentages in equal distances, is much better than the conical horn in certain respects. For example, the impedance " looking out " of a hole 0·7 inch diameter in an infinite plane wall, which is variable with frequency, reaches 80 per cent. of its ultimate value at a frequency of 9,300 cycles per second ; a certain conical horn applied to the hole brings this 80 per cent. value at 4,200 cycles ; and a comparable exponential horn brings it at 250 cycles. The horns do not alter the ultimate impedance of the hole in the wall. As a consequence, a horn is treated as having an impedance equivalent to that of an infinite cylindrical tube of diameter equal to that of the small end of the horn for air vibrations of frequency above a certain lower " cut off " limit, which is determined by the geometrical figure and dimensions of the horn. The impedance of an infinite cylindrical tube is, of course, a pure resistance, as energy passes along it from the source, undisturbed by reflections from the end.

---

[*] *Proc. Nat. Acad. Sci.*, 58, 63 (1915).

[†] See Section 12.

11. The Reproduction of Sound. One of the many interesting applications of these new methods of viewing acoustic problems is in the rendering of music and speech by the gramophone. As is well known, the vibrating parts of a gramophone comprise the needle, a lever, called the stylus lever, which rocks on a fulcrum, a diaphragm which forms the back of the sound-box, the air chamber of the sound-box, the tone arm and the horn. The three first-named items possess inertia and pliancy, and therefore contribute to the equations of motion of the system terms analogous to those introduced by inductance and capacitance into electrical equations ; the other items contribute only a resistance. The easiest way of utilising this analogy is to represent the inertia of each part by a suitable inductance coil, its pliancy by a condenser, and its power of consuming energy without phase change by a resistance. The chain of mechanical vibrating elements is thus replaced by a chain of inductances and condensers, terminated by a resistance. The properties of these electrical chains have been worked out, and the mathematical requirements for ensuring the easy passage of vibrations from element to element, without reflection at the junctions, are known. Hence can be deduced immediately the appropriate mass and pliancy of the stylus arm, of the diaphragm, and of the sound chamber, for the efficient co-operation, over a large range of frequencies, between these elements and the energy-consuming " load " imposed by the tone arm and horn. The result has been a notable improvement in both output and quality of the gramophone.

Within the past few years much attention has been paid to the optical recording of sounds. In one method, the sounds are recorded by transverse vibrations, such as the transverse movement of a spot of light over a photographic film, but this method is not suitable for reproduction. Rankine * used a different method, producing fluctuations in a beam of light. Light from a point source was collected by a lens, and an image formed on a small concave mirror, attached to the diaphragm of a gramophone recorder. The light then diverged, and passed through a similar lens which projected it to the distant station. Two similar grids were mounted, one in front of each lens, and an image of the first grid was superposed on the second by reflection in the concave mirror. When the latter oscillated, under the vibrations of speech, the dark spaces of the image moved over the openings of the second grid, thus producing fluctuations of the intensity of the beam. The light was received by a collecting lens, and focussed on a selenium cell, in circuit with a battery and receiver. In a later development the light was concentrated on a narrow slit, an image of which was produced by means of an auxiliary lens on a strip of cinematograph film, the slit image being transverse to the film. The variations in intensity of the light, when sound waves were received by the instrument, were recorded as variations in the density of the film, after development. For reproduction of the sounds, light from an illuminated slit was focussed on the film, behind which a selenium cell, connected to a telephone, was placed. As the film moved, the intensity of the light reaching the cell varied in accordance with the density of the film, and the corresponding sound was heard in the telephone.

This principle is now used in phonofilms,† but a sensitive type photo-electric cell replaces the selenium cell, since the latter lags. The current fluctuations through the photo-electric cell are amplified, and pass on to a loud speaker. The sound is recorded on the same film, and at the same time, as the cinematograph picture, so that perfect synchronisation between the picture and the sound is insured.

12. Wave Filters. It is well known that unless special precautions are taken, the passage of an electric current along a long telephone line, or cable, is accompanied by a distortion of the wave-form, due to the distributed electrical capacity of the line filtering out certain frequency components from the wave during transmission. By distributing inductance and capacity in the line it is possible to transmit certain selected ranges of frequency with negligible attenuation, all other frequencies being almost entirely suppressed. Such an arrangement is known as a *wave filter*. Once sounds are converted to currents this apparatus can be employed to sift out, and purify, sounds of various frequencies.

---

* *Proc. Phys. Soc.*, 31, 242 (1918); 32, 78 (1919).

† See Elwell, *Wireless World and Radio Review*, 15, 466 (1925); also *Bell System Tech. Journ.*, 8, 48 (1929).

Let us consider an electric wave filter consisting of equal electrical impedances * in series, divided into sections by electrical impedances in shunt branches, as shown in Fig. 19. The current in its passage from A to G is attenuated, some frequencies more than others. Let Z_1 denote each series impedance, and Z_2, the shunt impedance, and let the line B D F H be without impedance. The currents in the various parts are I_{m-1}, I_m, *etc.* Applying Kirchhoff's laws to the mesh C E F D,

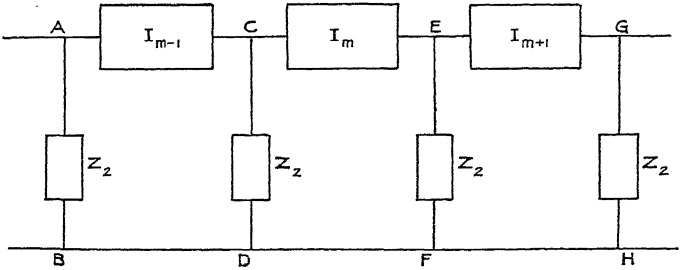


FIG. 19.—Electric wave filters.

$$Z_1 I_m + Z_2(I_m - I_{m+1}) = Z_2(I_{m-1} - I_m),$$

or,

$$\frac{I_{m-1}}{I_m} + \frac{I_{m+1}}{I_m} = 2 + \frac{Z_1}{Z_2}.$$

---

* If an electrical circuit consists of a resistance R in series with an inductance, L, and a capacity, C, the impedance is equal to $(R + pL - 1/pC$ where $p = 2\pi n$, n being the frequency alternation of the current.

Let us call the ratio of these successive currents e^{λ}, where λ is unknown, but in general is complex. Thus we have:

$$e^{\lambda} + e^{-\lambda} = 2 + \frac{Z_1}{Z_2},$$

i.e.,

$$\cosh \lambda = 1 + \tfrac{1}{2}\frac{Z_1}{Z_2}.$$

If λ is purely imaginary, the currents in adjacent sections differ only in phase. If λ is real, the current is diminished in transmission, the diminution obviously occurring away from the input end. If λ is purely imaginary, since $\cosh i\lambda = \cos \lambda$, where $i = \sqrt{-1}$,

$$+1 > \left(1 + \tfrac{1}{2}\frac{Z_1}{Z_2}\right) > -1,$$

and hence the limiting values for no attenuation are determined by the following:

$$\frac{Z_1}{Z_2} = 0,$$

$$\frac{Z_1}{Z_2} = -4.$$

Thus there is no attenuation within a range of frequency corresponding to these limits, and they define the extent of the frequency transmission band, the particular frequency range transmitted being determined by the values of Z_1 and Z_2.

Let us consider some types of such wave filters. Suppose Z_1 consists only of an inductance, L, and Z_2 only of a capacity, C. Then, $Z_1 = pL$, $Z_2 = -1/pC$, and,

$$\frac{Z_1}{Z_2} = -p^2LC.$$

When $$\frac{Z_1}{Z_2} = 0,\ p_1 = 0,\ n_1 = 0,$$

and if $$\frac{Z_1}{Z_2} = -4,\ p_2 = \frac{2}{\sqrt{LC}},\ n_2 = \frac{1}{\pi\sqrt{LC}},$$

where n_1 and n_2 are the frequency limits of transmission. Thus such a filter transmits all frequencies between zero and 1 and is known as a *low-pass filter*.

Similarly, if $Z_1 = -1/pC$ and $Z_2 = p\mathrm{L}$, the series impedances being equal capacities, C, and the shunts equal inductances, L, we have $Z_1/Z_2 = -1/LCp^2$, so that if

$$\frac{Z_1}{Z_2} = 0, p_1 = \infty, n_1 = \infty,$$

and when

$$\frac{Z_1}{Z_2} = -4, p_2 = \frac{1}{2\sqrt{LC}}, n_2 = \frac{1}{4\pi\sqrt{LC}}.$$

This filter, known as a *high-pass* one, transmits all frequencies from $1/4\pi\sqrt{LC}$ to infinity.

If each Z_1 and Z_2 consists of an inductance and the capacity in series, $Z_1 = (pL_1 - 1/pC_1)$ and $Z_2 = (pL_2 - 1/pC_2)$ so that:

$$\frac{Z_1}{Z_2} = \frac{pL_1 - 1/pC_1}{pL_2 - 1/pC_2}.$$

If

$$\frac{Z_1}{Z_2} = 0, p_1 = \frac{1}{\sqrt{L_1C_1}},$$

and when

$$\frac{Z_1}{Z_2} = -4, p_2 = \sqrt{\frac{4C_1 + C_2}{C_1C_2(L_1 + 4L_2)}}.$$

Such a filter transmits only between certain finite values of the frequency n, where $p = 2\pi n$, and is known as a *band-pass filter*.

These electric wave filters suggested to Stewart * the possibility of analogous effects in acoustics, subject to the following limitations and suppositions. The length of any selected section of an acoustic line—corresponding to an electric line—is so small in comparison with a wave-length that no change in phase occurs therein. By *acoustic line* is meant a bounded region of fluid, or solid, forming a tube or channel, and capable of transmitting sound waves only in the direction of the tube or channel. *Acoustical impedance* is the ratio of the maximum pressure difference applied to the maximum rate of change of volume displacement. When complex notation is used for simplicity, as in the alternating current theory, the acoustic impedance is the complex ratio of the pressure difference applied and the rate of change of volume displacement. The mathematical procedure is based upon three hypotheses: (1) the rate of volume displacement in any selected portion of the line, with a harmonically varying applied-pressure difference, can always be expressed by Ie^{jpt}, where I is complex; (2) the product of acoustic impedance and rate of volume displacement in any selected portion of the line equals the difference of pressure applied; (3) the algebraic sum of the volume displacements at any junction of lines is zero.

---

* *Phys. Rev.*, **20**, 528 (1922).

In the case of electrical oscillations:

$$L\frac{d^2Q}{dt^2} + R\frac{dQ}{dt} + \frac{Q}{C} = E \cos pt,$$

Q is the electric charge, R, the resistance, E, the maximum value of the applied potential difference, and the other symbols have their aforementioned meaning.

For sound, if we have a vibrating piston, as it were, of area S, it carries with it a volume of medium Sx, where x is the displacement, and the force acting on it is SP, where P is the pressure. Thus, in the case of sound vibrations, if m is the mass of medium vibrating:

$$\frac{m}{S}\frac{d^2x}{dt^2} + \frac{k}{S}\frac{dx}{dt} + \frac{fx}{S} = PS$$

where k is the damping and f, the stiffness. Comparing these two equations, we find that m/S^2, termed the *inertance*, is equivalent to the inductance L, and S^2/f, termed the *compliance*, is equivalent to the capacity C. Substituting these values of inertance and compliance for the inductance L and capacity C, respectively, in the equations for the electrical filters, the analogous equations for sound filters are obtained.

On account of the uncertainty as to whether an arrangement, say a tube, may be considered as having the equivalent inertness and compliance connected in parallel or in series, the application to actual cases is somewhat empirical. For instance, in the case of a closed chamber, or resonator, *e.g.*, Helmholtz's resonator, they are in series, and since the impedance in the corresponding electrical circuit is $(pL - 1/pC)$, the mechanical impedance is given by :

$$\frac{pm}{S^2} - \frac{f}{pS^2}.$$

In the Helmholtz resonator the mass m is that of the air piston in the neck, $m = \rho S^2 l$, where l is the length of the neck, S, its cross-sectional area, and ρ, the density of the air. The stiffness, f, is that of the air in the cavity, $f = S_0 \delta p$, and the frequency of the resonator is, remembering that the corresponding electrical frequency is $1/2$ [illegible]

$$\frac{1}{2\pi}\sqrt{\frac{f}{m}},$$

which agrees with the result obtained by other methods.

In practice low-frequency pass filters may be made by two concentric cylinders, joined by walls equally spaced, and perpendicular to the axis. Each chamber thus formed has a row of apertures in the inner cylinder which serves as the transmission tube. In one case * the volume of each chamber was 6·5 c.c., the radius of the inner tube 1·2 cm., and the length between apertures, 1·6 cm. A chamber and one such length of the inner tube is called a section. Four such sections were found to transmit 90 per cent. of the sound from frequency zero to frequency approximately 3,200, where the attenuation became very high, resulting in zero transmission up to about frequency 4,600, when transmission again appeared. High-frequency pass filters were made with a straight tube for transmission and short side tubes. The single-band filters constructed were a combination of the other two types, having side tubes leading to chambers of considerable volume. Such filters exhibited the same variations from theoretical performance as would be expected from a combination of the other two types, but the agreement of each type with theory is sufficient to enable filters to be designed to fulfil set conditions.

---

* See Stewart, *loc. cit.*

All these acoustic wave filters differ in principle from the ordinary resonance filter, such as a Helmholtz resonator. They do not depend upon resonance itself, but upon the interaction between recurrent similar sections of a transmission line, these sections containing the elements upon which free vibrations are to depend, and having over-all dimensions that are small in comparison with a wave-length of the sound.

Stewart's theory assumes lumped acoustic impedances in the main and branch lines, postulating that the air in each section of the filter moves as a whole, and that the length of each is short compared with one wave-length of the sound. Recently, Mason * has worked out a more general theory of the acoustic filter and has applied it to several special cases. Lindsay † has investigated the relation between the two theories, and he shows that, as far as the low-pass and single-band type filters are concerned, the lumped-impedance theory is as good in practice as Mason's theory. The weak point of Stewart's theory is the high-frequency pass for which his formulæ are semi-empirical.

BIBLIOGRAPHY

DAVIS and KAYE. "Acoustics of Buildings."
FLETCHER. "Speech and Hearing."
Physical Society's Report on Audition, 1931.
STEWART and LINDSAY. "Acoustics."
WATSON. "Acoustics of Buildings."
WOOD. "Sound."

---

* *Bell System Tech. Journ.*, 6, 258 (1927).
† *Phys. Rev.*, 34, 652 (1929).

CHAPTER V

LOW TEMPERATURES

1. The International Temperature Scale. Experience has for many years past indicated the necessity, for industrial purposes, of international agreement on a scale of temperatures, ranging from that of liquid oxygen to that of luminous bodies. The International Temperature Scale * adopted does not purport to replace the absolute temperature scale, but is intended merely to represent the absolute temperature scale in a practical manner with sufficient accuracy to serve the everyday needs of the laboratories.

The basic points of the scale are: (*a*) temperature of equilibrium between liquid and gaseous oxygen at the pressure of one standard atmosphere (oxygen point), —182·97° C.; (*b*) temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure (ice point), 0·00° C.; (*c*) temperature of equilibrium between liquid water and its vapour at the pressure of one standard atmosphere (steam-point), 100·00° C.; (*d*) temperature of equilibrium between liquid sulphur and its vapour at the pressure of one standard atmosphere (sulphur point), 444·60° C.; (*e*) temperature of equilibrium between solid silver and liquid silver at normal atmospheric pressure (silver point, 960·50° C.; (*f*) temperature of equilibrium between solid gold and liquid gold at normal atmospheric pressure (gold point), 1,063·00° C. Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm. high, having a mass of 13·5951 gm. per c.c., subject to a gravitational acceleration of 980·665 cm. per sec. per sec., and is equal to 1,013,250 dynes per sq. cm.

The means available for interpolation divide the scale into four parts: (1) From the ice point to 660° C. the temperature is d from the resistance R_t of a standard platinum-resistance meter by means of the formula $R_t = R_0\,(1 + At + Bt^2)$. The constants R_0, A and B are to be determined by calibration at the ice, steam, and sulphur points, respectively. The ratio R_t/R_0 is not to be less than 1·390 for $t = 100°$ C. and 2·645 for $t = 444·6°$ C. (2) From $-190°$ C. to the ice point the temperature t is to be deduced from the resistance R_t of a standard platinum-resistance thermometer by means of the formula :

---

* See text in *Bureau of Standards Scientific Papers*, **1**, 635 (1928).

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3].$$

C is to be determined at the oxygen point. (3) From 660° C. to the gold point the temperature t is to be deduced from the electromotive force, e, of a standard platinum-rhodium thermocouple, one junction of which is kept at a constant temperature of 0° C., while the other is at the temperature t, to be defined by the formula $e = a + bt + ct^2$. (4) Above the gold point the temperature t is determined by the ratio of the intensity J_2 of monochromatic visible radiation of wave-length λ cm., emitted by a black body at a temperature t_2, to the intensity J_1 of radiation of the same wave-length, emitted by a black body at the gold point, by means of the formula :

$$\log\frac{J_2}{J_1} = \frac{C_2}{\lambda}\quad 1{,}336 \qquad (t + 273)\Big].$$

C_2 is taken as 1·432 cm. per degree. The equation is valid for values of $\lambda(t - 273)$ of less than 0·3 cm. per degree.

In addition to the basic fixed points, the temperatures of a number of other points are available, and may be used in the calibration of secondary temperature-measuring instruments. These points and their temperatures on the International Scale are listed below :—

Temperature of equilibrium between solid and gaseous carbon dioxide	$-78·5°$ C.
,, of freezing mercury	$-38·87°$ C.
,, of transition of sodium sulphate	32·38° C.
,, of condensing benzophenone vapour	217·96° C.

Temperature of freezing cadmium	320·9° C.
,, ,, lead .	327·3° C.
,, ,, zinc .	419·45° C.
,, ,, antimony	630·5° C.
,, ,, copper in a reducing atmosphere . .	1,083 C.
,, ,, palladium . .	1,555 C.
,, of melting tungsten . . .	3,400 C.

Tests are now being made in various countries to determine what change, if any, must be made in the temperature scale used at the various laboratories.

2. Very Low Temperatures. The lowest temperatures are attained by allowing liquid helium to evaporate at reduced pressure. Onnes,* who originated this very low temperature technique, estimated that the lowest temperature he attained was some hundredths of a degree below 0·9° K.

An idea of the limit of these low temperatures is obtained by expressing the lowering of temperature as the ratio in which the absolute temperature has been decreased. Thus, passing from room temperature to that of liquid helium, evaporating under a pressure of 0·2 mm. of mercury, means a lowering in the ratio 250 to 1, and from the melting point of hydrogen to the helium-temperature 1·15° K., one of 13 to 1. The lowering from 1·15° K. to 0·82° K. is only one of 1·4 to 1, and a further reduction of 1·2 to 1 would be nearly the limit attainable with liquid helium. If it is considered that our knowledge of atomic structure renders it improbable that another substance will be discovered, or obtained in another way, more volatile than liquid helium, then the limit indicated, from which the lowest temperature yet attained is separated by only such a small amount, would seem an absolute one as regards the obtaining of lower temperatures. Such a limit, however, can only be accepted as a provisional one.

Keesom † has found that with the installation now in use in the Cryogenic Laboratory in Leiden, it is possible to make measurements at a temperature of about 0·85° K. in a space of about 300 sq. cm.

---

* *Trans. Farad. Soc.*, **18**, 145 (1922).

† *Comm. Phys. Lab. Leiden*, No. 195.

Keesom * solidified helium by subjecting the gas at very low temperatures to high pressures. He also determined the melting-point temperatures of the solid helium at different pressures. The results obtained are shown in Table I. If these results are plotted, the resulting curve bends at the lowest temperatures so as to become more and more parallel to the temperature axis. It shows no tendency at all to meet the vapour pressure curve at the triple point, as is usual with all other substances. Thus co-existence of solid and gas is not possible; there is no sublimation curve, and evaporation of the solid into the gaseous state will not be possible at these temperatures. The solid will always melt first.

TABLE I. MELTING-POINT TEMPERATURE OF SOLID HELIUM

Melting-point Pressure (Atmospheres) .	140·5	81·5	48·6	29·8	27·4	26·5	25·3
Temperature, K .	4·21°	3·12°	2·40°	1·83°	1·60°	1·42°	1·19°

There is yet another peculiarity which distinguishes helium from all other substances. According to Clapeyron's equation:

$$(v_2 - v_1)dp/dT = L/T,$$

where v_2 and v_1 are the specific volumes of the liquid and solid states, respectively, dp/dT is the variation of pressure and melting-point temperature, L, the latent heat of the substance, and T, the absolute temperature. Thus, the fact that the value of dp/dT of the melting-point temperature-curve of solid helium tends to zero indicates that the latent heat of fusion approaches zero value in a higher power of T than the first. This is in good agreement with Nernst's Heat Theorem.

It is interesting to compare the results given in Table I. with those obtained by Kamerlingh Onnes and Gulik † for solid hydrogen, shown in Table II.

---

* *Comm. Phys. Lab. Leiden.*, No. 184.
† *Ibid.*, No. 184.

TABLE II. MELTING-POINT TEMPERATURE OF SOLID HYDROGEN

Melting-point Pressure (Atmospheres)	53·5	44·9	37·7	23·4	14·2	5·2
Temperature, K	15·63°	15·38°	15·16°	14·71°	14·40°	14·11°

If the curve is plotted, the triple point, $p = 0{\cdot}07$ kgm. per sq. cm., $T = 13{\cdot}95°$ K., lies on it produced. Also from the curve obtained it follows that $dp/dT = 33$, and the melting-point pressure, corresponding to the critical temperature for liquid hydrogen, is 600 kgm. per sq. cm.

3. The Measurement of Very Low Temperatures. The practical methods of measuring low temperatures depend upon a knowledge of the temperatures of certain standard fixed points on the gas scale, such as the boiling-points of liquid oxygen, nitrogen, hydrogen and helium. These temperatures are as follows * :

Oxygen	−183·00° ±0·02 C.
Nitrogen	−195·81° ±0·02 C.
Hydrogen	−252·78° ±0·02 C.
Helium	−268·78° C.,

reduced to the thermodynamic scale of temperature. If the formula connecting the variation of vapour pressure with temperature is known over a temperature range, and the vapour pressure can be measured, we have a convenient method of determining very low temperatures. Over the range −183° to −205° C. the variation of the boiling-point temperature of oxygen with pressure is given by :

$$\log p_{mm} = -379{\cdot}95/T - 0{\cdot}0096219T + 1{\cdot}75 \log T + 4{\cdot}53939,$$

where $T = 273{\cdot}20 + t$, t being in ° C.

For nitrogen :

$$\log p_{mm} = -\ 301{\cdot}91/T - 0{\cdot}0090272\ T + 1{\cdot}75 \log T + 4{\cdot}17643.$$

For helium, where $T > 2{\cdot}190°$ K.,

$$\log_{10} p_{mm} = -\ 3{\cdot}024/T + 2{\cdot}208 \log_{10} T + 1{\cdot}217 \quad . \quad . \quad (1)$$

If $T < 2{\cdot}190°$ K.,

$$- 0{\cdot}922\ \log_{10} T + 2{\cdot}035 \quad . \quad . \quad (2)$$

---

* See Henning and Heuse, *Zeits. f. Phys.*, 23, 105 (1924) ; Keesom, Weber and Norgaard, *Comm. Phys. Lab. Leiden*, No. 202 ; Heuse and Otto, *Ann. d. Phys.*, 9. 486 (1931).

For the measurement of very low temperatures, at which the vapour pressure of helium approaches a very small value, no thermometer except helium gas thermometers, with the gas at very low pressure, can be used, as the pressure must in any case remain below the vapour pressure corresponding to the temperature to be measured. All measurements of temperature in this region have to be reduced to readings on a helium thermometer, supposed to be filled with the gas at normal temperature and pressure.

Onnes and his co-workers found that a Knudsen gauge was the most satisfactory arrangement for measuring these low vapour pressures. Two types of gauge are available, the hot-wire and the absolute gauge.*

With the hot-wire type the heat conducted away from an electrically-heated wire is proportional, approximately, to the gas pressure in the vessel containing the wire. The value of this heat conduction can be obtained directly from the current passing along the wire and the potential difference between the ends of the wire. Provided that the distance between the wire and the walls of the vessel is small, compared with the mean free path of the gas molecules, the heat conducted away from the wire depends only on the nature of the gas, the difference of temperature between the wire and the walls, the gas pressure and the surface areas of wire and walls. Although the loss of heat from the wire may be taken as approximately proportional to the gas pressure, a calibration is usually required, since there is in general a deviation from proportionality, due to heat flowing off at the ends of the wire.

Now, if a vessel containing vapour at room temperature is connected by means of a tube to another vessel containing vapour and liquid in equilibrium at a known low temperature, a pressure difference exists between the two vessels. This is due to *thermal transpiration*, and must be taken into account whatever manometer is used. Fortunately, this difficulty, inherent in the measurement of pressures at low temperatures, can be avoided by the use of the hot-wire manometer, as it is possible to keep the manometer vessel itself at a temperature but little above that of the evaporating helium, of which the temperature is to be measured, by immersing it in the helium bath.

---

* See Newman, "Production and Measurement of Low Pressures," p. 151.

At first sight, owing to superconductivity,* it seems doubtful whether the principle on which the manometer is based, *viz.*, a change of resistance with temperature, can be applied at such low temperatures. But it appears that the resistance remaining at this temperature is still sufficient (if an appreciable current flows through the wire) to heat the latter, until the temperature is reached at which the resistance begins to increase, and so the influence of the gas pressure on the loss of heat from the wire becomes observable from the difference of current necessary to maintain the same resistance.

In Table III. the vapour pressure of helium vapour over liquid helium is given, together with the corresponding temperatures, deduced by means of equations (1) and (2). In all cases the low temperatures were produced by evaporation of the liquid helium, the vapour being drawn off by powerful pumps.

TABLE III. VAPOUR PRESSURE OF HELIUM AT DIFFERENT TEMPERATURES †

Vapour Pressure p cm. of Mercury.	Temperatue T°K.	Vapour Pressure p cm. of mercury.	Temperature T°K.
132·9	4·899	0·500	1·538
76·00	4·219	0·250	1·393
50·00	3·795	0·1000	1·237
25·00	3·218	0·0500	1·139
10·00	2·636	0·0250	1·055
5·00	2·298	0·0100	0·960
2·50	2·013	0·0050	0·899
1·000	1·714	0·0025	0·844

Another suitable thermometer for the measurement of low temperatures is the thermo-couple. A gold-silver couple may be used down to the temperature of liquid hydrogen, and even down to the higher helium temperatures it shows a fairly large thermo-electric power.* At the lower helium temperatures, however, the thermo-electric power diminishes rapidly, so that this couple is insensitive at temperatures below about 4·2 K. Moreover, it is not at all free from disturbing electromotive forces, which appear at places of great fall of temperature in cryostats. Couples of iron-constantan, or of copper-constantan, can be used down to 18° K.

---

* See Section 13, Chapter VIII.

† See Keesom, Weber and Schmidt, *Comm. Phys. Lab .Leiden*, No. 202.

Kamerlingh Onnes and Holst † have shown that the thermo-electric power of all the couples investigated approaches zero value at helium-temperatures. The various wires, iron, silver, gold, platinum, lead and constantan, were measured against copper. The results are shown in Table IV., where *T* is the temperature of one junction, that of the second junction being 16° C.

TABLE IV. THERMO-ELECTRIC FORCE IN VOLTS × 10^6 OF METALS (MEASURED AGAINST COPPER)

T	Ag.	Au.	Pt.	Pb.	Fe.	Constantan.
81° K	−28	−129	−298	−457	+1293	−432
20°	−28	−282	−68	−553	+1319	−819
4·26°	−21	−375	−58	−559	+1309	−990
3·20	—	−383	−59	—	+1309	−1002
2·26°	—	−386	—	—	—	−1004

Platinum and other resistance thermometers are convenient for use at low temperatures. Henning and Heuse ‡ have shown that between 0° C. and −193° C. the resistance of platinum can be represented accurately by a formula of the type :

$$R_t = R_0 (1 + at + bt^2 + ct^4).$$

For one of Henning's standard thermometers the co-efficients had the values indicated by the following equation :

$$\frac{R_t}{R_0}$$

---

* See Kamerlingh Onnes, *Comm. Phys. Lab. Leiden*, No. 142.

† *Ibid.*, No. 142 (c).

ts. f. Phys., 23

where R_t is the resistance at $t°$ C. and R_0, that at 0° C. Below about —193° C. the platinum thermometer becomes insensitive. Kamerlingh Onnes and Holst made a series of determinations of the change of resistance with temperature of different metal wires down to helium temperatures in order to find a metal, or an alloy, which could be used as a resistance thermometer at the lowest temperatures. Constantan shows a considerable decrease of resistance at decreasing temperatures. The resistance of manganin also diminishes considerably, and in an approximately linear manner, with temperature, from the temperature of liquid oxygen down to that of liquid helium. Hence wires of manganin may be used, equally well as wires of constantan, as resistance thermometers even at the lowest temperatures.

One difficulty with these wires is that the ice-point resistance does not remain constant ; after cooling it often appears that a discontinuous change has taken place. Magnetic fields also cause disturbances. Thus, Keesom and van den Ende * found that the resistance of a constantan wire undergoes a relatively large change under the influence of a magnetic field, and that this change does not entirely disappear on switching off the field. These investigators looked for other alloys on which magnetic fields have no such disturbing influences. They investigated the following alloys : platinum-silver, platinum—10 per cent. iridium, brass, phosphor-bronze and technically-pure platinum. The resistances were measured at the temperatures of melting-ice, liquid air, liquid hydrogen and liquid helium.

The wires, Pt.-Ag., Pt.-Ir., and technically-pure Pt., all of diameter 0·05 mm., showed a continual change of resistance with temperature, but in the region of liquid-helium temperatures the change was too small for the wires to be used as thermometers. The results are shown in Table V.

Brass showed, down to the temperatures of liquid hydrogen, a continuous change of resistance with temperature. In liquid helium, however, its resistance almost entirely disappeared. Nevertheless, the residual resistance appeared to be still dependent on the temperature.

* *Comm. Phys. Lab. Leiden*, No. 203.

TABLE V. CHANGE OF RESISTANCE OF METAL WIRES WITH TEMPERATURE

T°K.	R/R_0.				
	Pt.-Ag.	Pt.-Ir.	Pt.	Brass.	Phosphor-bronze.
83	0·9441	0·7748	0·4150	0·7710	0·8725
20·38	0·9243	0·7168	0·2627	0·7052	0·8558
4·17	0·9245	0·7147	0·2575	—	—
2·94	0·9240	0·7146	—	—	—
1·91	—	—	0·2572	—	—

The resistance of phosphor-bronze seemed to change nearly linearly with the temperature in the neighbourhood of that of liquid helium. The relative change in this temperature region is much larger than has previously been obtained for any other alloy; *e.g.*, it is about fifty-five times as large as for constantan, and the change of the resistance appears to be quite reproducible. The influence of a magnetic field of 150 gauss appears to be relatively small, and does not cause a lasting disturbance. Results were obtained as follows:—

T°K	4·218	1·383	1·089	1·060	1·033	0·995	0·994
R/R_0	0·7737	0·6588	0·6490	0·6474	0·6465	0·6470	0·6463

The resistance of a pre-annealed phosphor-bronze wire differed by little, at the temperature of liquid helium, from that in liquid hydrogen. Keesom and van den Ende concluded that phosphor-bronze, which has *not* been annealed, is extremely suitable for use as a thermometer in the neighbourhood of the temperature of liquid helium.

4. Specific Heats at Very Low Temperatures. The atomic heats at constant volume of simple substances * are given by an expression of the form:

where the function F is the same for all the substances, and Θ is a constant, characteristic of each substance. This result, obtained experimentally, has also been deduced by Debye * from the quantum theory. He regards a solid as a continuous elastic medium, and considers the vibrations of the solid body as a whole. The constant, Θ, is given by :

---

* The atomic heat is the product of the specific heat and the atomic weight.

where h is Planck's constant, k, Boltzmann's constant, and ν_m, the upper limit of the frequency vibrations of the continuous elastic solid. This upper limit is introduced because the medium has a discontinous, or atomic, structure. At very low temperatures the expression for the atomic heat takes the form :

$$12 \quad {}^4R \quad T^3$$

where R is the gas constant, so that at the lowest temperatures the specific heat at constant volume is proportional to the cube of the temperature. The value of Θ for a given substance can be calculated directly from the elastic constants of the solid.† Such a calculation involves no thermal measurements, and the agreement of the value deduced in this manner with the values required by the specific heat measurements is evidence for the correctness of the Debye theory.

Measurements of the specific heat of solids, at very low temperatures, are of special importance in view of Debye's theory of the T^3 law at these temperatures. Nernst and his collaborators measured the specific heats of metals, down to the temperature of liquid hydrogen, and Kamerlingh Onnes and Holst ‡ made preliminary measurements of the specific heat of mercury at liquid-helium temperatures. The method which is most suitable for low temperature calorimetry is one developed by Nernst and Eucken. A block of the metal to be investigated, provided with wires for heating and temperature measurement, is suspended in a vacuum, made as perfect as possible. Within the block a measured

---

* *Ann. d. Phys.*, 39, 789 (1912).

† See Roberts, " Heat and Thermodynamics," p. 401 (1928).

‡ *Comm. Phys. Lab. Leiden*, No. 142.

quantity of heat is developed by an electric current, and the increase of temperature thus produced is determined.

Kamerlingh Onnes and Holst found that for mercury over the range 2·93° K.—3·97° K., Θ was equal to 60, whereas over the range * 31° K.—301° K. the experimental value is 97. There is no discontinuity in the specific heat values at 4·19° K. such as is found in the values of the electrical resistance of mercury at this temperature (superconducting state).

Keesom and Kamerlingh Onnes † measured the specific heat of lead between 14° K. and 80° K., and also of copper over the range 15° K.—22° K. Taking Θ for lead equal to 88, the experimental curve shows good concordance with the one calculated from Debye's formula over the whole range, but there are deviations to the extent of about 4 per cent. at 30° K. The values of the specific heat of copper appeared to follow Debye's law over the temperature range 15° K.—22°K.

Later, Keesom and Kamerlingh Onnes ‡ determined the specific heat of copper between 14° K. and 90° K. A small deviation from the T^3 law was observed, the deviation being in the sense that, at decreasing temperature, the atomic heat decreased more rapidly than it should according to the T^3 law. In the region of the temperature of liquid hydrogen, and above it up to 40° K., the values of Θ decreased continually. In this respect the behaviour of copper differs from that of lead. For the latter metal the values of Θ increase with increasing temperature in the liquid hydrogen region, and begin to decrease beyond about 30° K.

Keesom and van den Ende § have measured the specific heat of lead and bismuth over the range 2° K.—17° K. To a first approximation the results agreed very well with the Debye-curve over the whole temperature range investigated. The apparatus and arrangement used are shown in Fig. 20.

Two copper cylinders, C_1 and C_2, were screwed one in the other. The inner cylinder was closed by a copper plate, C_3, which carried two tubes, N_1 and N_2 of German silver and a lead tube, L.

---

* See Pollitzer, *Zeits. f. Elektroc.*, 19, 513 (1913).

† *Comm. Phys. Lab. Leiden*, No. 143.

‡ *Ibid.*, No. 147.

Ibid., No. 203.

The temperature wire, A_1, was of annealed constantan, of which the resistance-temperature variation is more reproducible than that of constantan which has not been annealed. The helium was admitted through the tube L, which was afterwards sealed off.

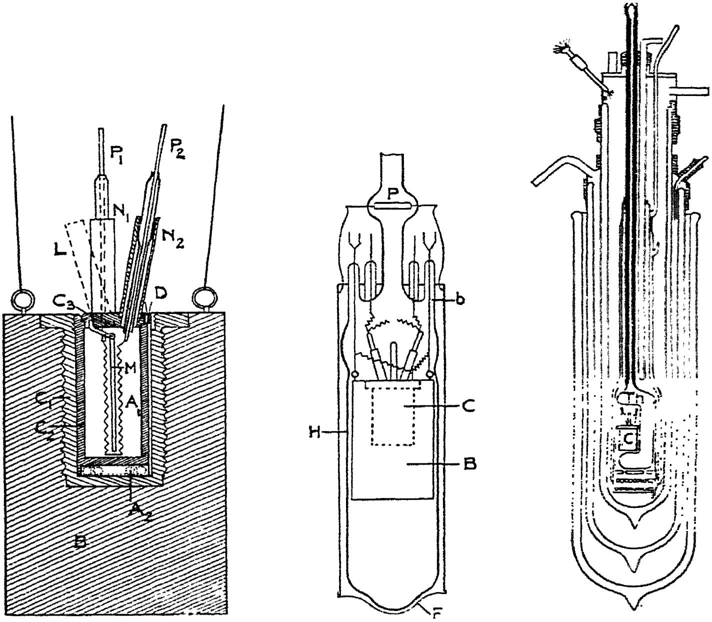


FIG. 20.—Measurement of the specific heats of solids at very low temperatures.

P_1 and P_2 were platinum leads to the thermometer. The wires D led to the heating coil, the latter being within the space below the inner cylinder of the core. The core C, together with the metal block B to be investigated, were suspended inside a glass vessel.

The heat insulation required special care, and to protect against heat radiation, the glass vessel was silvered. To shield off radiation from above, the platinum plate, P, was placed in the exhaust tube, and maintained at the temperature of the bath by wires, which led to the copper enclosure, H. The latter also protecting against heat radiation, was closed at the bottom by tinfoil, F. The whole was placed in a liquid helium cryostat, and by means of diffusion pumps the liquid helium was evaporated so that temperatures down to 2° K. were obtained.

To a first approximation the results for lead in the liquid-helium temperature range, and in the range between liquid-helium and liquid-hydrogen temperatures, agree with a Debye-curve, Θ being equal to 88. Absolute agreement with one single Debye-curve could not, however, be obtained. At lower temperatures the atomic heat corresponds with smaller calculated values of Θ, and at temperatures below 7° K. the Θ's show rather large fluctuations. Yet they seem to change linearly with the temperature in the entire temperature range (7° K. $\Theta = 83$, 16° K., $\Theta = 86$). This agrees with the results of Keesom and Kamerlingh Onnes.* The measurements show definitely that the course of the specific heat curve of lead does not change abruptly when the metal becomes superconducting.

The curves for bismuth correspond with the value $\Theta = 96$. To a first approximation, the results again agree with a Debye-curve, though here also deviations occur. There appears to be a minimum, with $\Theta = 92$ at about 9° K.; from here the Θ values increase continuously, $\Theta = 103$ at 3° K. and $\Theta = 104$ at 20° K. The value for bismuth, calculated by Debye † from elasticity measurements, is $\Theta = 111$.

Some of the results obtained are given in Table VI.

Recently, Clausius and Vaughen ‡ have measured the specific heats of thallium, calcium and magnesium down to 10° K. The behaviour of magnesium is anomalous in that the value of Θ increases below 30° K., implying a failure of the T^3 law for which no explanation is apparent.

5. The Thomson Effect at Low Temperatures. Until recently, very few direct determinations of the value of the Thomson

---

* *Comm. Phys. Lab. Leiden*, No. 143.

† *Ann. d. Phys.*, 39, 817 (1912).

‡ *Journ. Amer. Chem. Soc.*, 52, 4686 (1930).

TABLE VI. ATOMIC HEATS OF LEAD AND BISMUTH

Temperature. °K.	Lead.		Bismuth.	
	Θ	Atomic Heat.	Θ	Atomic Heat.
3	81·4	0·0233	103·3	0·0114
4	81·8	0·0545	101·0	0·0286
6	82·5	0·178	96·1	0·112
8	83·3	0·406	92·4	0·300
10	84·2	0·726	92·3	0·567
12	85·1	1·09	94·3	0·860
14	86·0	1·53	96·6	1·17
16	86·9	1·91	99·0	1·49
18	87·8	2·25	101·5	1·78
20	88·7	2·62	104·1	2·05

coefficient at low temperatures had been made. Borelius, Keesom and Johansson,* using wires of copper and silver alloyed with small quantities of gold, measured it at the temperature of liquid hydrogen. These wires were then used as "normals" for indirect determinations of σ (Thomson coefficient) in a number of pure metals, the value of the Thomson coefficient being calculated from the equation $\sigma = \sigma_{\text{norm.}} + T.de/dT$, where e is the thermoelectric force, per degree, against the normal wire with a known Thomson coefficient ($\sigma_{\text{norm.}}$) and T, the absolute temperature. The pure metals investigated were Cu, Ag, Au, Fe, Pd, Pt, Pb, Ni and Co, all having cubic structure; Zn and Cd, hexagonally crystallising metals; alloys, including binary alloys of Cu, with small quantities of Fe, Co, Ni, Pd, As and Au; binary alloys of Pt and Rh; and a ternary Pt, Pd, Au alloy. The results show that in general there is a tendency towards verification of the limiting laws: $\sigma \rightarrow 0$ and $e \rightarrow 0$ for $T \rightarrow 0$, but experiments at still lower temperatures will be necessary to obtain conclusive results.

BIBLIOGRAPHY

ROBERTS. Heat and Thermodynamics.

* *Comm. Phys. Lab. Leiden*, Nos. 196, 206.

CHAPTER VI

ELECTROMAGNETIC RADIATIONS

1. The Range of Electromagnetic Radiations. Electromagnetic radiations range in wave-length from the very long wireless waves, 18 km. is the wave-length of certain transatlantic signals, down to about 10^{-13} cm. or less, the estimated wave-length of the cosmic rays, recently discovered by Millikan. Over this whole range of wave-lengths there is a continuous spectrum of radiations of which visible light occupies a very small band, 8×10^{-5} cm.—4×10^{-5} cm.

The electric waves extend from well over 10^6 cm. in an unbroken spectrum down to 10^{-2} cm. Overlapping the electric waves are the heat waves, or infra-red region, 3×10^{-2} cm.—8×10^{-5} cm., followed by the visible region of the spectrum. The latter is overlapped by the ultra-violet rays and these reach well into the region occupied by X-rays, although the gap between the ultra-violet rays and the X-rays was only closed fairly recently by the soft X-rays. Beyond the X-ray region come the γ-rays from radioactive bodies, followed by the cosmic rays which have the shortest wave-length of any known electromagnetic radiations.

2. Electric-Waves. One of the most interesting features connected with electric waves is their bending around the earth, which is now attributed to refraction by ions in the air. Ions are known to be present in the air at the earth's surface, and there is every reason to suppose that their number increases with altitude. Although it is difficult to compute this ionic distribution, different estimates all agree in predicting that the increase in the number of ions, present in the atmosphere, with altitude is so rated, that we pass almost discontinuously from an atmosphere which may be treated as an insulator to a region that is a relatively good conductor. This region is known as the Kennelly-Heaviside layer and acts somewhat like a mirror, reflecting the electric waves back to the earth. Since the latter also acts as a reflector, the waves are thus reflected between the two surfaces, which we may imagine to function as two concentric spherical mirrors.

Now the boundary of the Kennelly-Heaviside layer can scarcely be sharp enough to permit of true reflection. Probably what occurs is a continuous bending of the rays by refraction throughout their whole path, as shown in Fig. 21. This ionic refraction is explained by the fact that the velocity of propagation is greater in the ionised layer. Plane wave-fronts are therefore bent forwards in their upper portions, so that the waves can finally reach the earth again.

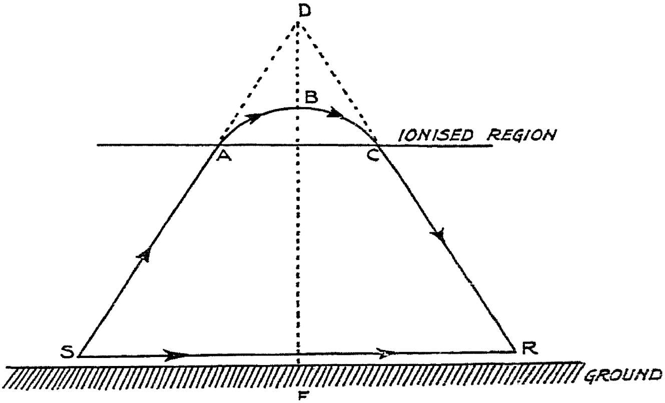


FIG. 21.—Refraction of wireless waves.

Suppose that the waves are transmitted between S and R, where S is the transmitter and R the receiver. The waves reach R by at least two paths.* One of these paths, SABCR, constitutes the *atmospheric wave*, the other, SR, follows the ground and is called the *ground wave*. When the two waves meet at R they interfere, and slight changes in the effective path-lengths cause the interference to be sometimes additive and sometimes destructive. In this manner " fading " is produced.

---

* See Appleton, *Proc. Phys. Soc.*, **41**, 43 (1928) ; Eccles, *Proc. Roy. Soc., A*, **87**, 79 (1912).

Various direct methods have been proposed for determining the " effective height " of the Kennelly-Heaviside layer. One of the earliest methods involved a change in the wave-length of the waves.*

Let the optical path difference between the two waves, ground and atmospheric, be D, where D is, in general, a function of the wave-length of the radiation. Then

$$\mathrm{n} = D/\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of wave-lengths the atmospheric waves are behind the ground waves at R, and λ is the wave-length of the waves *in vacuo.* Further,

$$D = \int_{SBR} n\, ds - \mathrm{SR},$$

where n is the refractive index at any point, and ds is an element of length of the atmospheric ray path.

The experimental procedure consists in measuring the variation in n, as shown by the signal current maxima and minima experienced at R, as λ is continuously varied through a small range. From equation (1) we have,

$$\delta \mathrm{n} = - D\delta\lambda/\lambda^2 + \delta D/\lambda.$$

Usually δD is neglected and $\lambda^2\delta\mathrm{n}/\delta\lambda$ taken as the equivalent path difference, from which the equivalent height of the deviating layer can be obtained.

For short waves, where the influence of the earth's magnetic field can be neglected, $U = cn$, where U is the group velocity of the waves and c the velocity of the waves in free space. Under such conditions the equivalent path of the atmospheric ray would be

$$\int \frac{ds}{n} = c \int \frac{ds}{U}.$$

It has been shown by Breit and Tuve † that $\int \frac{ds}{n}$ is equal to

---

* See Appleton and Barrett, *Nature*, 115, 334 (1925).

† *Phys. Rev.*, 28, 571 (1926).

(SD + DR), in which case DE is the equivalent height of the layer. For medium wave-lengths, 100 to 1,000 metres, the quantity $\int \frac{ds}{U}$ is not necessarily equal to $\int \frac{ds}{n}$, but it has been customary to calculate the equivalent height for these wave-lengths in the same way. In both cases, therefore, the calculation proceeds as if the atmospheric ray path consisted of two straight lines, and the deviation at the layer were brought about by sharp reflection.

The angle of incidence of the downcoming atmospheric waves has been determined by Appleton and Barrett * and by Smith-Rose and Barfield.† From the value of the angle, the effective height of the layer can be determined by a simple calculation. Thus,

$$n \sin \theta = \sin \theta_0.$$

Where θ is the angle the atmospheric ray makes with the vertical at any point at which the refractive index of the medium is n, and θ_0 is the experimentally-determined angle of incidence at the ground. This is equal to the angle of incidence at the layer, assumed horizontal. So if,

$$U = cn,$$

and since

$$dx = ds \sin \theta,$$

$$c\int \frac{ds}{U} = \int \frac{ds}{n} = \int \frac{dx}{\sin \theta_0} = (\mathrm{SD} + \mathrm{DR}),$$

where dx is measured horizontally.

A method, known as the group-retardation method, of obtaining the equivalent height of the layer was first introduced by Breit and Tuve.‡ They sent out short pulses of wireless waves and measured the time interval, δt, between the arrival of the signal pulses, received *viâ* the ground and *viâ* the atmosphere. For such a case,

$$\delta t = \int_{SBR} \frac{ds}{U} - \int_{SER} \frac{ds}{U'}, \quad . \quad . \quad . \quad . \quad (2)$$

---

* *Proc. Roy. Soc., A*, **109**, 621 (1925).
† *Ibid.*, **110**, 580 (1926) ; **116**, 682 (1927).
‡ *Loc. cit.*

where U' is the group velocity of the waves along the ground. If $U' = c$, $c\int \frac{ds}{U}$ is determined and is equal to the path SDR.

The average heights of the layer, obtained by these various methods, agree fairly well, although the departure from the average is much greater in the case of observations made by the angle of incidence method than in the case of those made by the other methods. This difference can perhaps be explained by assuming that reflection does not always take place at a point mid-way between the two stations, in which case we infer that the layer cannot always be regarded as horizontally stratified.

Appleton, using 400-metre waves, found that after sunset the equivalent height increased slowly, reaching a maximum value, averaging 126 kilometres, at about 30 to 40 minutes before sunrise, after which a rapid reduction in height took place. This variation suggests that the upper atmospheric ionisation is produced by some type of solar radiation. On the cessation of the influence of this radiation after sunset, recombination of ions would cause a slow increase in the height of the layer to take place, which would only cease on the advent of sunrise, at the height of the lower boundary of the ionised region. The renewed action of this radiation causes a rapid fall of the layer, as deduced from measurements of the equivalent height, and confirmed by observations on fading, which show that the optical path of the atmospheric waves is being steadily reduced. The reduction in the intensity of the atmospheric waves, which takes place after the height of the layer has fallen to an approximately constant value, appears to be due to the absorptive action of an ionised region, say D region, formed below the normal deflecting region, E region. There is also a certain amount of evidence which suggests that on certain occasions, after sunrise, measurable reflection takes place from the D region, as well as from the E region.

Although the type of nocturnal variation described above may be regarded as normal, in some cases the changes in equivalent height were not so marked, while in other observations much greater and more complicated variations were measured. Sometimes the equivalent height remained approximately constant at about 100 to 110 km. In other cases, during the winter months, abnormally great equivalent heights have been recorded.

More recently, Appleton and Green,[*] using 100-metre waves, have found evidence of the existence of two deflecting regions, E and F, the equivalent heights of which were about 100 km. and 230 km. during the daytime. The lower region, E, was found to reflect only in the daytime. The 100 metres seems to be a critical wave-length in that on some days waves of this length will penetrate the E region, while on others the waves are reflected by the same region, whereas the wave-lengths of 200 and 400 metres are always reflected by this region during the daytime. Now it is known that 100-metre waves require an electron density of about 10^5 electrons per c.c. to reflect them, so it seems probable that this represents the maximum ionic density in the E region.

Lugeon's[†] results indicated the presence of ionised layers at 280, 185, 85 and 50 km., when the Kennelly-Heaviside layer was at a height of 83·6 km. at Zurich and 110 km. at El Goleá, where his experiments were made. All these layers do not reflect simultaneously. At night the waves are reflected by the highest layer, but during the day mainly by the lowest layer.

Breit, Tuve and Dahl,[‡] working with 75-metre waves, obtained results corresponding to layer heights at 105, 235 and 470 km., respectively. Appleton explains these results on the double-region hypothesis, the two regions, E and F, having equivalent heights of 105 and 235 km. In the majority of their recorded tests in daytime, Breit, Tuve and Dahl obtained reflection corresponding to heights of 235 and 470 km., the reflection from the lower height of 105 km. being missing. This is to be expected since 75-metre waves require a greater electronic density to deflect them than do 100-metre waves, so that with the shorter waves reflection by the E region should not be so frequent.

Larmor[§] has shown that when the simultaneous effects of the electric force in the waves and the earth's magnetic force on the electrons in the Kennelly-Heaviside layer, are taken into account, the passage of waves of about 214 metres wave-length will produce violent vibration of the electrons; the wave propagation will, therefore, be most strongly influenced for waves of this wave-length, and a particularly strong absorption of these waves will result. The phenomenon is analogous to anomalous dispersion in the case of optics, the centre of the absorption band corresponding, approximately, to 200 metres. There is thus a radical change in the behaviour of wireless waves when the wave-length of 200 metres, or so, is exceeded. The magnetic field of the earth is not constant, but varies from point to point, and so the critical, or resonant, frequency, *i.e.*, when the frequency of the waves is equal to that of the electrons, is not the same at different points in the path.

---

[*] *Proc. Roy. Soc., A*, **128**, 159 (1930).

[†] *Comptes Rendus*, **191**, 676 (1930).

[‡] *Proc. Inst. Rad. Eng.*, **16**, 1236 (1928).

[§] *Phil. Mag.*, **48**, 1025 (1924).

Recently Merritt * has studied what may be termed the fine structure of a wireless wave front. He used two coils as receivers, placed at two points on the same wave front about half a wave-length apart, the signals being brought by means of cables to a cathode-ray oscillograph. He arranged that one signal produced a horizontal vibration of the spot of light, while the other produced a vertical vibration, the amplitude and phase relations between these vibrations being the same as between the original magnetic fields at the two receivers. It is to be expected that at two points on the same wave front, the phase and amplitude would be the same, and so the figure in the oscillograph should be a straight line at 45° to the horizontal. Usually, such a figure was not observed. In general, it was an ellipse which changed from moment to moment, both in size and shape. At times, the changes occurred so rapidly, and so erratically, that it was quite impossible to follow them.

Merritt explains these effects as follows: Assuming that waves reach the receiving apparatus by several different paths, it is to be expected that they will differ in amplitude, phase and direction, so that an interference pattern will be formed at the receiver. The pattern, if conditions are steady, will consist of a fixed system of interference bands. When the conditions for radio-reception are bad, it is probable that there are effects going on in the upper atmosphere which destroy any constancy of either amplitude, or phase, at the receiver. We may compare this destruction to the destruction of the interference pattern on a Michelson interferometer, which we can imagine would take place, if the interferometer were placed in strong convection currents in heated air. Patterns would still be obtained, but the character of the pattern would vary from instant to instant, and so no definite pattern could be detected.

From what has been said previously, the effect of the Kennelly-Heaviside layer is to produce *wireless echoes, i.e.*, two signals—or sometimes more than two—are received for each single signal transmitted. Thus the dot of the Morse Code is received as two dots. When signals are received from a powerful short-wave station, capable of transmitting over great distances, another type of echo is frequently observed, in which the separation between the signal and its echo is of the order of one-seventh of a second. This has been explained by supposing that one signal has come by the shortest path, while the other has travelled round the world, and reaches the receiving station from the opposite direction. The time interval between the reception of the signals has been carefully measured, and the consistent results obtained enable one to estimate the height at which the waves travel. In some cases, however, these " round the world " echoes are accompanied by echoes having a retardation considerably less than one-seventh of a second—sufficiently long to permit the waves to travel two or three thousand miles but not much further. These echoes may be produced by waves which have reached the observer after reflection from a hillside, or possibly from the waves of the ocean.

Another type of echo is one which occurs with a retardation ranging from three seconds to nearly thirty seconds. This time-interval corresponds to a distance range of five million miles. In practice, signals were sent out at intervals of thirty seconds from Eindhoven in Holland, and were received independently by three observers, two at different stations in Eindhoven and one in Oslo, Sweden. In most cases the echoes were received at all three stations if received at one, and frequently the echo was observed at all three stations and with nearly the same retardation.

Two suggestions have been put forward to explain these long-interval echoes. One is that at times there is a stream of electrons from the sun at a distance of a million miles, or so, from the earth, which is sufficiently dense to reflect the waves. Such an electron stream would be bent by the earth's magnetic field, so as to have a tendency to reflect the waves directly back to the earth. Secondly, it has been suggested that the waves do not leave the earth at all, but travel in a region of the atmosphere where the conditions are such as to make the group velocity extremely small.

The general belief is that the ground wave is guided by the earth in much the same way that an alternating current is guided by a wire. Within the immediate neighbourhood of the sending station there seems to be little doubt that this view is correct, but it is uncertain to what distance this mode of propagation extends. There are some facts which are more readily accounted for if we think of the wave along the ground as proceeding according to optical laws along a curved path, which rises to only a relatively small height above the earth.

3. Ultra-short Electric Waves. Nichols and Tear [*] attempted to join up the infra-red and electric-wave regions of the spectrum. The electric wave receiver used was a modified form of the Nichols' radiometer; the usual blackened vanes were replaced by heater elements made of very thin deposits of bright metallic platinum on thin mica strips; when electric waves fell on these, they caused oscillatory currents of the same frequency in the platinum surfaces, and part of the energy was converted into heat. The oscillator was in principle the familiar Hertzian doublet with minute tungsten cylinders. A Boltzmann and a Fabry Perot interferometer were employed in wave-length measurements. The latter gave the approximate wave-form, and accurate values of the wave-lengths. Waves were measured down to 0·220 mm., or shorter than the longest known heat waves.

Glagolewa-Arkadiewa,[†] using as oscillators finely-divided metallic particles suspended in a viscous oil, obtained waves as short as 0·082 mm.

---

[*] *Nat. Acad. Sci. Proc.*, **9**, 211 (1923); *Astrophys. Journ.*, **61**, 17 (1925).

[†] *Nature*, **113**, 640 (1924).

Stable oscillations may be obtained down to about 2 metres wave-length by using a standard type of thermionic valve, and simply reducing the constants in conventional oscillatory circuits. Below this wave-length major difficulties appear. A special type of oscillator was developed by Barkhausen and Kunz * ; the usual plate and grid potentials were reversed in polarity, a high positive voltage being applied to the grid and a smaller negative, or zero, potential to the plate. It was found that this connection could be used to produce extremely high frequencies, wave-lengths of the order of 0·5 mm., or less, being obtained. Gill and Morrell † used a circuit of this variety, the values of the inductance and capacity in the external circuit controlling the frequency.

Recently ‡ a 5-metre oscillator, using 10 kw., has been constructed, which showed remarkable effects. Current-measuring instruments in neighbouring rooms were burnt out, and observers noted that their body temperature rose, the temperature of the blood actually rising slightly.

Busse § has obtained a radiation of 50 watts on a wave-length of 28·6 cm., using shock excitation from high-frequency sparks.

The Lecher wire system is the most satisfactory method of measuring the wave-length of these short waves.

4. Infra-red Spectra. The infra-red region of the spectrum has recently attracted much attention, most of the work being done in what is termed the *near infra-red*, for which the region is usually taken as that lying from the end of the visible spectrum, at about 7,500 Å., or 0·75 μ, equivalent to a wave-length of 0·00075 mm., as far as 23 μ, this being the limit of usefulness of dispersing prisms. Beyond this, in the *far infra-red*, coarse gratings have been employed, but for the most part reflection from polished plates of crystals, the method of *Restrahlen*, up to 200 or 300 μ, as developed by the school of Paschen and Rubens, is used. The most exhaustive description of practical work, using dispersing prisms, has been given by Robertson and Fox, ‖ and the use of tings is discussed very fully by Snow and Taylor.* The apparatus used by the latter is shown in Fig. 22. For a short distance beyond the visible red, photography has been employed, but even with specially sensitised plates, the limit is little beyond 1 μ. By making use of the evaporation of naphthaline on a celluloid film, Czerny † has recently succeeded in photographing bands up to 6 μ. As the phosphorescence, induced in certain preparations of zinc sulphide containing definite impurities, is quenched by infra-red radiation, this method has also been tried for the detection of emission and absorption bands, but the results, while interesting, are somewhat lacking in definition, at least as regards absorption.

---

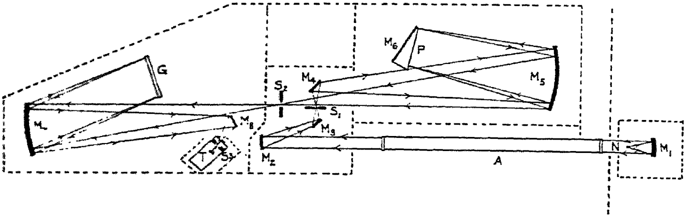
* *Zeits. f. Phys.*, **21**, 1 (1920).

† *Phil. Mag.*, **49**, 369 (1925).

‡ *Journ. Frank. Inst.*, **209**, 473 (1930).

§ *Zeits. f. Hochfrequenz. techn.*, **31**, 97 (1928).

‖ *Proc. Roy. Soc.*, **120**, 128 (1928).



N = Nernst filament.
A = Gas absorption tubes.
M_1 M_2 M_5 M_7 = Concave mirrors.
M_3 M_4 M_6 M_8 = Plane mirrors.
Position of screens shown thus - - - -

S_1 S_2 S_3 = Slits.
P = Rock salt prism.
G = Grating.
T = Thermopile.
Path of rays shown thus ←

FIG. 22.—Investigation of infra-red spectra by means of a grating.

Considering first the theoretical aspect of infra-red spectra, Drude,‡ from the phenomenon of dispersion in crystals, showed that if any position be chosen for a wave-length in the ultra-violet there must be a corresponding wave-length in the infra-red. Electrons are concerned in the ultra-violet region and all recent work confirms that the band spectra, found in the infra-red region, arise from atoms and molecules. These are treated, in the first instance, as rigid bodies possessing internal and rotational energy, either or both of which may vary, giving rise to emission or absorption of energy in the form of radiation. The fundamental assumptions are those employed by Bohr in his theory of line series, namely,

---

* *Proc. Roy. Soc.*, 124, 442 (1929).
† *Zeits. f. Phys.*, 53, 1 (1929).
‡ *Ann. d. Phys.*, 14, 677 (1904).

(1) The emission of a frequency, ν, is due to a decrease, $h\nu$ (h is Planck's constant) in the energy of the radiating system.

(2) If the system is in rotation, and is not emitting radiation, its angular momentum must be an integral multiple of $h/2\pi$. There is thus a limited number of possible angular velocities.

Hence, in the infra-red the spectra indicate transitions in the oscillations of the atoms of a molecule and transitions in the rotation of the molecule itself. As the effect is one of resonance, the atoms in a molecule respond in their vibration to radiation possessing some particular frequency. The electronic linking between the atoms prevents their oscillation from being truly sinusoidal, and so harmonics may be expected and are, in fact, found. Electronic transitions are, for the most part, detected by effects in the visible, or the ultra-violet regions, but as contributions of all three types of energy, electronic, oscillatory and rotational, interact, there may be found in the infra-red-spectrum evidence of electronic charges.

5. Oscillation Bands. In the early work the bands in the infra-red were evident as maxima of emission, or absorption. When plotted on an energy-frequency, or energy-wave number, basis, the bands look the form of smooth peaks, the maxima of which were, as a rule, fairly well defined. The experimental results showed that in many cases these bands are harmonics of a fundamental frequency, this harmonic relationship being explained somewhat as follows : When radiation falls on the molecule, it is absorbed in quanta, $h\nu$, according to the characteristic frequency of the vibrating components, and further, as the nuclei are not removed sufficiently far from one another to obey a pure sine law defining their period, the departure from this law permits of a Fourier analysis. Thus the vibration is resolved into a fundamental and harmonics, representing one, two, three quanta, *etc.*

6. Rotation Bands.* Molecules also undergo rotation, and this effect is reflected in their infra-red spectra. Consider the case of a diatomic molecule of moment of inertia I rotating with angular velocity, ω, about an axis perpendicular to the line joining the atoms. Taking the moment of momentum as a whole multiple of $h/2\pi$ (*i.e.*, quantising the moment of momentum),

---

* For an account of the analysis of band spectra see Curtis, *Proc. Roy. Soc., A*, 101, 38 (1922) ; Jevons, *Proc. Phys. Soc.*, 41, 538 (1929) ; Dennison, *Rev. Modern Physics*, 3, 280 (

$$I\omega = \frac{mh}{2\pi}, \text{ and } E = \frac{h^2}{8\pi^2 I} m^2,$$

where m is any positive integer and E, the kinetic energy of the molecule. If E and E_1 represent the kinetic energy of the molecule in two states corresponding to m and m_1 we have :

$$h\nu = E - E_1 = \tag{3}$$

By the principle of selection m can change by ± 1, or 0, so that :

The frequency of the light emitted is thus $\nu = \frac{h}{8\pi^2 I}(2m - 1)$ when m is positive, and $\nu = -\frac{h}{8\pi^2 I}(2m + 1)$ when m is negative. The frequencies emitted are, therefore :

m .	3	$+2$	$+1$		-1	-2	-3 . . .
ν .	$5c_o$				c_o	$3c_o$	$5c_o$, . . .

where $c_o = h/8\pi^2 I$. The frequency $- c_o$ for $m = 0$ indicates an absorption of energy by the molecule. The spectrum should therefore consist of lines with frequencies c_o, $3c_o$ $5c_o$, *etc.*, a series of equally spaced lines, and from existing data in connection with molecular moments of inertia (of the order of 10^{-40} for the lighter molecules) we conclude that the lines must lie in the far infra-red, round about 30 μ. In spite of the great difficulties attending work in this region a certain amount of evidence, confirmatory of the theory, has been obtained, *e.g.*, for water-vapour absorption.

More recently half-quantum numbers have been introduced, *i.e.*, $m - \frac{1}{2}$ is written for m. This leads to the formula :

$$\nu = \frac{h}{8\pi^2 I}(2m),$$

which contains no constant term. In some cases no constant term is found, *e.g.*, for HCl rotation bands,* pointing to the existence of half-quantum numbers.

7. Oscillation-rotation Bands. The bands in the near infra-red, and especially those towards the visible region of the spectrum, possess a fine structure. The calculations of the previous section can now be applied, so far as rotation is concerned, to the fine structure found in these oscillation-rotation bands. If we suppose that the molecule vibrates with a frequency, ν_0, then as a decrease, $h\nu_0$, in the internal energy may occur simultaneously with the change in angular momentum, the frequencies which will be emitted when the oscillation and rotation energies both change will be given by :

$$\nu = \nu_0 + \frac{h}{8\pi^2 I}(\pm 2m-1), \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

assuming that the moment of inertia remains unchanged. Such a formula would indicate a fundamental ν_0 and harmonics. The frequencies emitted are :

m	3	2	1	0
ν	$\nu_0 + 5c_0$ $\nu_0 - 7c_0$	$\nu_0 + 3c_0$ $\nu_0 - 5c_0$	$\nu_0 + c_0$ $\nu_0 - 3c_0$	$\nu_0 - c_0$ $\nu_0 - c_0$

The fundamental frequency, ν_0, is invariably absent from the spectrum, and often one or more of the adjacent lines, $\nu_0 + c_0$, *etc.*, are also suppressed. The absence of the former has been attributed to the non-existence of molecules having no rotational energy, which would obviously be the only ones capable of giving rise to it. This explanation would at the same time account for the absence of the adjacent lines. On the other hand, it may be that the non-rotating molecule is capable of existing, but incapable of emitting its characteristic frequency ν_0, without a simultaneous change in its angular momentum.

---

* See Czerny, *Zeits. f. Phys.*, **34**, 227 (1925).

It has been assumed so far that the moment of inertia remains unchanged during energy changes, but the latter are bound to cause a change in the value of I, so that if I_1 denotes the final moment of inertia after the energy change, equation (3) becomes :

$$h\nu = E - E_1 = \frac{h^2m^2}{8\pi^2 I} - \frac{h^2m_1{}^2}{8\pi^2 I_1}.$$

If $m \longrightarrow (m - 1)$ we have, taking the oscillation and rotation energies into account,

$$h\nu = h\nu_0 + \frac{h^2m^2}{8\pi^2 I} - \frac{h^2(m-1)^2}{8\pi^2 I_1},$$

i.e., $$\nu = \nu_0 - \frac{h}{8\pi^2 I_1} + \frac{hm}{4\pi^2 I_1} + \frac{h}{8\pi^2}\left(\frac{1}{I} - \frac{1}{I_1}\right)m^2$$

or, writing $c_0{}'$ for $\frac{h}{8\pi^2 I_1}$ and c_2 for $\frac{h}{8\pi^2}\left(\frac{1}{I} - \frac{1}{I_1}\right)$,

$$\nu = \nu_0 - c_0{}' + 2c_0{}'m + c_2m^2. \quad . \quad . \quad . \quad . \quad (5)$$

Similarly, if $(m - 1)$ increases to m,

$$\nu = \nu_0 + c_0 - 2\,c_0m + c_2m^2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where c_0, as before, is equal to $\frac{h}{8\pi^2 I}$.

If the angular momentum remains unaltered during the energ change $h\nu_0$, the frequency emitted will be modified in consequenc of the change in the moment of inertia, and so for $m \longrightarrow m$,

$$\nu = \nu_0 + c_2m^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7$$

Many bands are represented by equations (5), (6) and (7), whic represent three series, forming three branches of the band. Thes branches are known as the *positive*, *negative* and *zero branche* respectively, or the R, P and Q branches. They are defined a follows :—

Positive branch, R . $\nu = \nu_0 - c_0{}' + 2c_0{}'m + c_2m^2$.
Zero (null) branch, Q . $\nu = \nu_0 + c_2m^2$.
Negative branch, P . $\nu = \nu_0 + c_0 - 2c_0m + c_2m^2$.

Only positive integral values are to be given to m.

8. Infra-red Spectra of Gases. For molecules of similar constitution, in which one atom increases progressively in mass, it is found that the predicted fundamental infra-red oscillation band of the series decreases in frequency with increasing atomic weight. Examples are found in the case of HF, HCl, HBr and HI, for which [*] the values of ν_0, are, respectively, 4003, 2939, 2590 and 2272 cm^{-1}, and of NH_3, PH_3, AsH_3, which [†] have for one of the fundamentals the wave numbers, 1630·9, 1125·0 and 1005·4 cm^{-1}, respectively. The frequency of rotation in a similar series of molecules slows down with increasing atomic weight of the characteristic atom.[‡]

The moment of inertia of a molecule, obtained from observations of the spacing of fine structure in the infra-red,[§] has been found to agree with the value as calculated by ordinary spectroscopic methods.

Barker and Meyer,[||] in a survey of the experimental investigations on the vibration bands of simple molecules in the gaseous state, propose a method of classification of molecules into groups according to the complexity of the rotational energies. Diatomic and linear molecules, like carbon dioxide and acetylene, only rotate in a plane and show no precession. Polyatomic molecules rotate with a precession, the complexity of which depends on the molecular symmetry.

In addition to the light which they throw on molecular structure, the infra-red bands of gases also afford other varied information. Thus infra-red data have been used to determine the quantity of radiation from the sun, stars and planets, and the temperatures prevailing in these bodies have thereby been deduced.

A knowledge of the infra-red spectrum of water vapour, and of carbon dioxide, is of importance in considering the nature and quality of energy reaching us from the sun. Simpson, making use of the absorption coefficients of water and carbon dioxide in the infra-red, has predicted that an increase in solar radiation would result in increased cloud and precipitation, and even in the apparent paradox of an ice age.

---

[*] See Czerny, *Zeits. f. Phys.*, **44**, 235 (1927).
[†] See Robertson and Fox, *Proc. Roy. Soc.*, *A*, **120**, 189 (1928).
[‡] *Loc. cit.*, Czerny.
[§] See Snow, Rawlins and Rideal, *Proc. Roy. Soc.*, *A*, **124**, 453 (1929).
[||] *Trans. Farad. Soc.*, **25**, 912 (1929).

9. Infra-red Spectra of Liquids. When salts, which easily form hydrates, such as $CaCl_2$, $Al_2(SO_4)_3$, *etc.*, are dissolved in water, the solution may be more transparent than water in certain parts of the spectrum. According to the solvate theory which has been put forward, the dissolved salts form slightly stable compounds with the water, which are more transparent to the infra-red than water, under the same conditions On the other hand, it has been suggested that there exist in water several kinds of molecules which possess different absorption bands. Neither theory, however, accounts for all of the observed results.

The infra-red spectra of liquids may be correlated with their chemical constitution. For example, the spectra of the primary alcohols,* *i.e.*, those which contain a CH_2OH group, are very similar up to about wave-length 10 μ, both in the position and intensity of the principal bands. On the other hand, beyond 10 μ, all of these spectra are distinguishable, one from the other.

The structure of a compound may be determined from a knowledge of its infra-red spectrum. For example, in the case of water of crystallisation, *e.g.*, in gypsum ($CaSO_4$, $2H_2O$), the principal water bands appear in the spectra, in some cases being superimposed upon the characteristic bands of the compound, which they completely mask. The occluded water behaves as though it were itself anisotropic in an anisotropic crystal, uniaxial in an uniaxial crystal, and biaxial in a biaxial crystal. On the other hand, with water of constitution, *e.g.*, manganite, $Mn(OH)_2$, all the water bands disappear, except the one of wave-length 3 μ.

The absorption spectra of organic liquids show numerous bands in the infra-red region below 3 μ. Now it is probable that most, if not all, of the fundamental absorption bands of hydrocarbons, which are associated with the fundamental vibration frequencies of the molecule, occur with wave-lengths greater than 3 μ and, accordingly, bands below 3 μ have been interpreted as having

---

* Sappenfield, *Phys. Rev.*, 33, 37 (1928); Smith and Boord, *Journ. Amer. Chem. Soc.*, 48, 1512 (1926).

overtone and *combination* frequencies. A striking example of this occurs in the case of benzene.*

There seems to be considerable similarity between the spectra of molecules containing CH and those containing NH groups. For associated with each type of group, or linkage as it is called, there appear to be two fundamental bands near wave-lengths 3·3–3·4 μ and 6·7–6·9 μ for CH, and near 3 μ and 6 μ for NH, the shorter wave fundamental in each instance having an *anharmonic series of overtones*, and the longer having few, if any, overtones.

10. Infra-red Spectra of Solids. The most sensitive method of investigating the infra-red spectra of solids is by means of absorption, or transmission. In general, the reflection method gives only the fundamentals, whereas if we know the absorption law of the solid, it follows that every absorption, however small, can be detected by using sufficiently thick pieces of the material in question, and not only can the fundamentals be found, but also all combinations. If one has measured the absorption and reflection spectrum of a substance—the latter giving only the fundamentals—then it is possible to express all other bands in terms of the fundamentals. If there remain bands which cannot be accounted for either as fundamentals, harmonics or combinations, then it is possible that there exists, also, a fundamental which is *inactive*, *i.e.*, an *imperceptible fundamental*.

Among the many very striking resemblances between the absorption spectra of salts may be mentioned that of different salts containing AX_4 groups. Tolksdorf † investigated the four salts, sulphate, chromate, perchlorate and permanganate of potassium. All four show a very intense absorption at positions not very far removed from wave-length 10 μ. In addition, there is an inactive fundamental associated with each group.

Taylor ‡ measured the absorption spectra of $KMnO_4$ in the infra-red and found a band at wave-length 12·7 μ. Further, the absorption spectrum was banded in the visible region. The frequency difference between these bands is the frequency of oscillation of the Mn atom, as determined from the infra-red spectrum. On dissolving the salt in water, the bands in the visible region were less widely spaced. This is attributed to the slowing down of the vibration of the Mn atom within the MnO_4 group, due to hydration of the negatively charged ion.

---

* See Ellis, *Trans. Farad. Soc.*, **25**,

† *Zeits. phys. Chem.*, **132**, 161 (1928).

‡ *Trans. Farad. Soc.*, **25**, 860 (1929).

Apart from the large amount of experimental work that has been done in the infra-red region, the ultra-violet and visible regions have also received much attention. For details of recent work the reader is advised to consult the report * on " Molecular Structure." The study of band spectra, in general, promises to be a valuable source of information about the masses and structure of the nuclei of atoms, and in particular seems likely to lead to the discovery of many new isotopes.† Already it has been established that there are oxygen isotopes of mass 17 and 18, and that carbon has an isotope of mass 13. It may be that all elements have isotopes, although the agreement of Aston's determinations with the usual atomic weights proves that any isotopes, as yet unknown, can only be present in very small amounts. For the detection of such isotopes, the analysis of band spectra seems superior to the mass spectrograph, although, as band spectra give only the relative masses of two isotopes, the two methods must be used to supplement each other.

11. The Application of Band Spectra to Two Types of Hydrogen. Wigner and Witmer ‡ have extended the wave mechanics of atomic spectra to molecular spectra, and have shown that at ordinary room temperatures hydrogen consists of two sets of molecules. In other words, there are two forms of hydrogen, *viz.*, *symmetric* (*para*) and *antisymmetric* (*ortho*). These theoretical considerations have received striking experimental confirmation.

Denison § has shown that calculations of the specific heat of hydrogen, on this basis, are in complete accord with fact. Hydrogen, which has been kept at very low temperatures for a long enough time, and then heated, should have a different specific heat curve, *i.e.*, the curve relating specific heat and temperature, from that obtained with normal hydrogen. This experiment has been made by Bonhoeffer and Harteck.* They succeeded in producing large changes in the properties of hydrogen by cooling it to liquid-air, or liquid-hydrogen, temperatures in the presence of charcoal. While the equilibrium ratio of symmetric (*para*) to antisymmetric (*ortho*) hydrogen at ordinary temperatures is 1 : 3, this becomes 1 : 1, approximately, at liquid-air temperatures, and at liquid-hydrogen temperatures, hydrogen in equilibrium should consist of nearly 100 per cent. symmetric molecules. Using charcoal as a catalyst, they prepared mixtures of symmetric and antisymmetric hydrogen, varying in composition from 25 per cent. to nearly 100 per cent. of the symmetric form. Some properties of the two forms and of ordinary hydrogen—the 1 : 3 mixture—are given in the following table :

---

* *Trans. Farad. Soc.*, 25, 611 (1929).

† See Birge, *ibid.*, 718 (1929).

‡ *Zeits. f. Phys.*, 51, 859 (1928).

§ *Proc. Roy. Soc.*, *A*, 115, 483 (1927).

	Symmetric (*para*) Hydrogen.	Antisymmetric (*ortho*) Hydrogen	Ordinary Hydrogen.
Triple point	13·83°K	13·99°K	13·95°K
Vapour Pressure at 20·39°K.	787 ± 1mm	751mm.	760mm.

The heat of vaporisation of the symmetric hydrogen is 0·65 per cent. less than that of the antisymmetric form. Independently, Eucken † secured an enrichment of the symmetric hydrogen by cooling hydrogen at high pressures to liquid-air temperatures, and has shown that the heat capacity of different samples, so treated, differs widely from that of ordinary hydrogen, in accordance with Denison's theory.

The transformation of *ortho-hydrogen* into *para-hydrogen* from the room-temperature equilibrium ratio of 3 : 1 toward the zero-degree equilibrium ratio of 0 : 1, actually proceeds very slowly, as is to be expected, in cold hydrogen gas, kept under very high pressures, so as to increase the frequency of molecular collisions. The changing ratio may be followed by means of the changing specific heat of the gas, which behaves like a mixture of two gases different specific-heat curves. An interesting result of this work is that, just as in cooling ordinary hydrogen below room temperature the 3 : 1 ratio is ordinarily preserved, so in warming hydrogen, which has been kept near 0° K. in charcoal, the 0 : 1 ratio, characteristic of the latter temperature, is preserved.

---

* *Zeits. phys. Chem.*, **4**, 113 (1929).

† *Naturwiss*, **17**, 182 (1929).

Clusius and Hiller [*] have described a relatively simple installation for preparing para-hydrogen in large quantities under pressure. They also evaluated the specific heats of liquid and solid para-hydrogen, and the heats of fusion. Within the limits of experimental error these quantities are in agreement with those of ordinary hydrogen. The specific heat of para-hydrogen exceeds, at 115° K., the classical value for the diatomic rotator, as predicted by the new quantum mechanics.

12. The Raman Effect. In recent years a large number of experiments have been made on the scattering of light by gases, solids and liquids,[†] and the most important discovery arising from this work is the *Raman effect*.

Raman [‡] found that when monochromatic light of a definite frequency was passed through organic liquids, such as benzene, toluene, *etc.*, the most intense line in the scattered light was equal in frequency to that of the incident light, as was to be expected on the classical theory, but, in addition, a number of new lines were observed on the low-frequency side of the main line, and a few fainter ones on the high-frequency side. These lines are often referred to as the *Stokes'* and *anti-Stokes' lines*, respectively, in analogy to similar lines in fluorescent spectra. By the process of scattering, a set of new discrete frequencies had thus made their appearance.

The magnitude of the change in frequency is found to depend upon the nature of the scattering material, and is independent of the frequency of the incident light. In general, each exciting line evokes several modified lines, some of which may be plane polarised.

The Raman effect is shown by many liquids, by gases under pressure and by transparent solids. The effect in the case of solids was discovered independently by Landsberg and Mandelstam,* who examined the light scattered by certain crystals. Such experiments are not easy, for the scattered light is feeble, and long exposures with intense sources of light are necessary to bring out the relatively faint new lines.

---

[*] *Zeits. phys. Chem.*, **4**, 158 (1929).

[†] See Raman, *Phil. Mag.*, 5, 498 (1928) ; *Proc. Roy. Soc., A*, **122**, 23 (1929).

[‡] *Indian Journ. Phys.*, **2**, 387 (1928).

Superficially, the Raman effect resembles fluorescence, but in the latter phenomenon the frequencies of the lines of the fluorescent spectrum are independent of those of the exciting lines, provided that the latter are able to excite fluorescence. But the frequencies of the radiations, modified by Raman scattering, are directly related to the frequency of the incident light. If this be ν, the frequencies of the new lines are $\nu - \nu_1$, or $\nu + \nu_1$, where the shifts, ν_1, are either actual infra-red frequencies in the absorption spectrum of the scattering substance, or differences in such frequencies. For example, among the lines emitted by a mercury vapour lamp, are those of wave numbers, 27,354, 27,290, 24,704 and 22,939 cm.$^{-1}$, which, when scattered by benzene molecules, give rise to Raman lines, including those of wave number 24,294, 24,231, 21,646 and 19,877 cm.$^{-1}$, respectively. Each of these has been shifted towards the red from the exciting line by an amount 3,060 cm.$^{-1}$, approximately, and corresponds to an infra-red wave-length 3·27 μ. The infra-red absorption spectrum of benzene includes a strong band at 3·25 μ.

The intensities of the Raman lines are of a different order compared with the lines in the fluorescent spectrum, and, in addition, many of them are strongly polarised.

With few exceptions, the displaced Raman lines correspond to observed infra-red bands, but there seems to be little or no correlation between the relative intensities of the displaced lines and the intensities of the corresponding infra-red bands. Thus benzene has a very strong absorption band at wave-length 9·75 μ, toluene one at 6·86 μ, and chlorbenzene at 6·77 μ, but Pringsheim † finds no evidence for any scattered lines displaced by the corresponding frequencies. In addition, the most intense Raman lines of these substances are displaced by frequencies corresponding to the 10·3 μ, 10·2 μ and 10·0 μ infra-red bands, respectively, which are not the strongest infra-red bands of the substances. It appears that we may have a Raman line corresponding to an infra-red transition which is forbidden by the selection rules, and we thus have the possibility of detecting energy levels of molecules which can only be found by the Raman effect. Langer* has utilised this principle in his work on the Raman effect in $C\,Cl_4$.

---

* *Naturwiss*, **28**, 557 (1928).

† *Zeits. f. Phys.*, **50**, 741 (1928).

Raman illuminated his fluids in spherical glass bulbs, concentrating the light of a mercury arc at the centre of the bulb, and photographing the illuminated area, viewed end-on. This method of excitation is very inefficient, although the mercury arc is still used extensively as a source of illumination for the excitation of the Raman effect. An improved form of apparatus with mercury excitation, as used by Wood,† is shown in Fig. 23 (*a*). He has also adopted the helium discharge as a source of radiation, employing the strong line, λ, 3,888·6 Å., Fig 23 (*b*). In the latter case the apparatus consists of a tube wound into a tight spiral, furnished with copper electrodes, and operated by a transformer giving 20,000 volts. Within this tube is a second one, open at both ends and transparent only to ultra-violet light. Inside this second tube is a third one of transparent glass, one end of which is flattened, ground plane, and polished, and the other end drawn off to an oblique funnel, painted black on the outside to provide a black background against which the excited liquid is viewed.

The apparatus for the excitation of the Raman effect in gases consists of a tube drawn off into a tapering cone at the rear, and constricted and expanded at the point. It is mounted over, and in contact with, a very long mercury-arc lamp. Hollow cylindrical reflectors enclose the two tubes. The illumination produced in this way is very intense, as the light from the lamp is beaten back and forth between the walls of the reflectors. The exposure may be shortened by having the gas under pressure.

In the case of solids the light from a mercury vapour lamp is directed by a large condensing lens on to a block of the material, and the light, scattered at right-angles, is focussed on to the slit of a spectrograph. It has been shown by Bär * and Menzies † that the Raman spectra of solids in powder form may be obtained, the incident radiation being much weakened by repeated reflections.

---

* *Nature*, **123**, 345 (1929).

† *Phil. Mag.*, **6**, 729 (1928) ; **7**, 744 (1929).

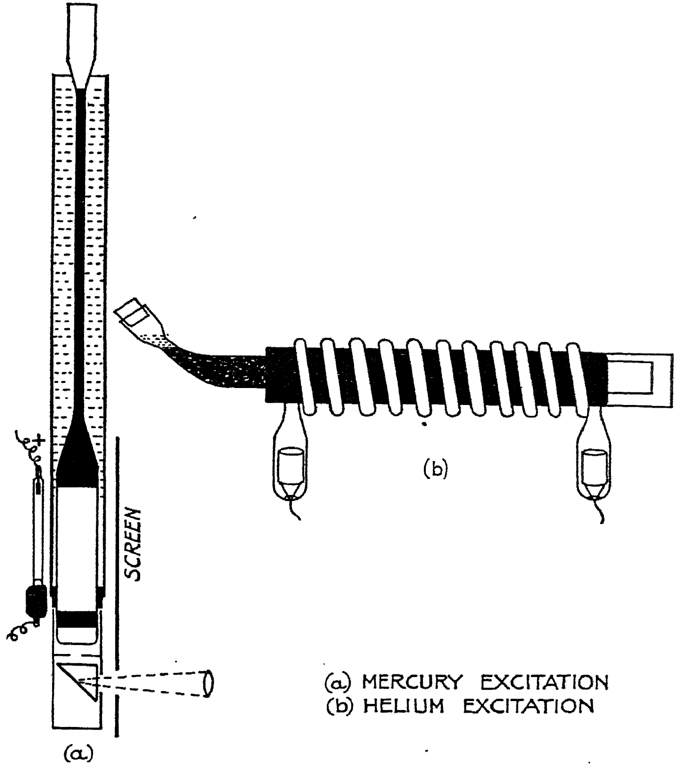


FIG. 23.—Raman effect technique.

---

* *Nature*, **124**, 692 (1929).
† *Ibid.*, **124**, 511 (1929).

This is an advantage, since only a few solids are obtainable in

The Intensity and Polarisation of Raman Lines. The intensity of the Raman lines increases rapidly with decreasing wave-length of the incident radiations. Experiment and theory have proved that the Stokes' lines, $\nu-\nu_1$, situated towards the red, are always more intense than the corresponding anti-Stokes' lines, $\nu+\nu_1$.

The anti-Stokes' lines or, as they are sometimes called, the *positive lines*, grow more intense as the temperature is raised * and, in addition, the shifted lines all move inward toward the position of the unshifted light as the temperature rises. Brickwedde and Peters † have studied the variation of the intensity of the Raman lines from quartz as a function of the temperature, using the λ, 2,537 Å., line of mercury. Their results are shown in Fig. 24 (*b*). The very broad black band is due to primary light (λ, 2,537 Å.) scattered without change of frequency. The lines marked S 21 μ and A 21 μ are Raman lines, corresponding to an absorption band at λ, 21·5 μ. The former are due to quanta which have spent part of their energy in exciting vibrations corresponding to λ, 21 μ, while the latter, A 21 μ, consist of quanta which have received energy from these vibrations. At 55° C. the Stokes' line, S 21 μ, is more intense than the mercury line, λ, 2,564 Å. At 300° C. they are of equal intensity, and at 525° C., the mercury line, λ, 2,564 Å., is more intense than S 21 μ. Thus the temperature variation of the Raman effect in crystalline media is different from that according to the classical theory of scattering which predicts an increase in intensity of the scattered radiation with the absolute temperature. If the Raman scattering were coherent, the intensity of the Stokes' line, S 21 μ, should increase with temperature, and it should be more intense than the mercury line, λ, 2,564 Å., at 525° C.

The fact that different lines are differently polarised is probably closely connected with the relative intensity of the Raman lines and the appearance, or non-appearance, of infra-red absorption

---

* See Krishnan, *Nature*, **122**, 650 (1928).

† *Bull. Am. Phys. Soc.*, **3** (1928).

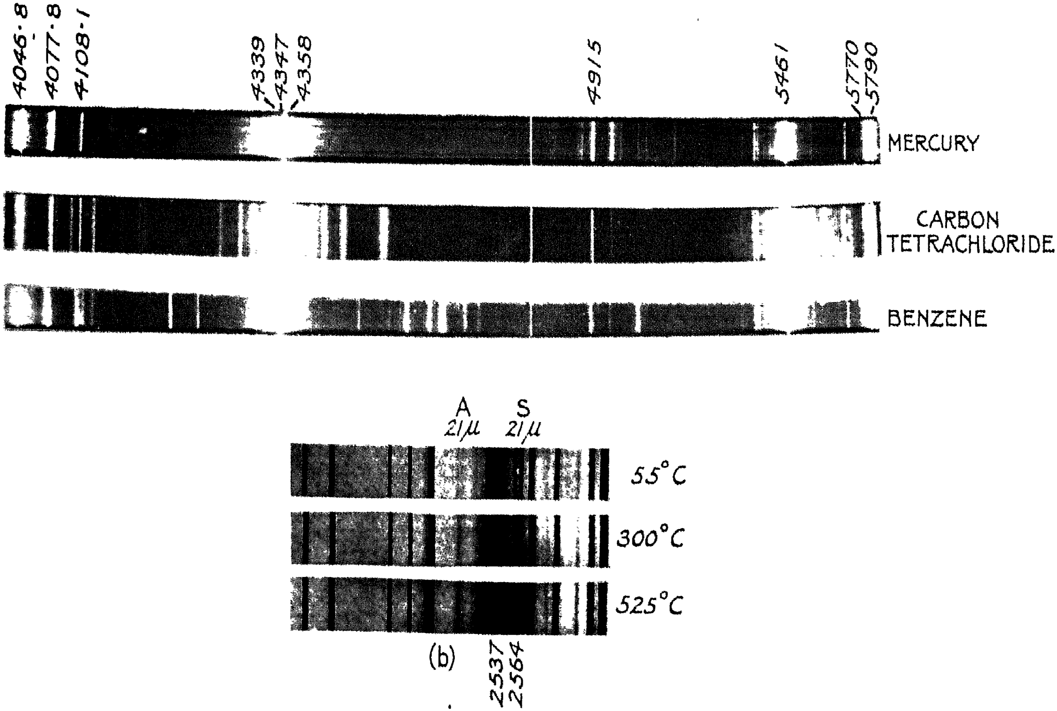


Fig. 24. The Raman effect.

lines. Results seem to indicate that, in liquids at any rate, the *depolarisation* [*] of the classically scattered light shows a very rapid increase as we approach the ultra-violet. The theory of anomalous dispersion leads us to anticipate the existence of such an effect.

Cabannes [†] found that the Raman lines in crystals (quartz and Iceland spar) are not all in the same state of polarisation, the intensity and depolarisation of the lines depending upon the orientation of the crystal.

Menzies [‡] has investigated the polarisation of lines in the spectra of light scattered by liquids, CCl_4, *etc.*, in a direction perpendicular to the incident beam and also in a direction obliquely forward. He concluded that many of the observed facts could be accounted for by considering the initial and final directions of vibration, in the molecule involved, to be parallel in the case of the polarised lines, perpendicular in that of the unpolarised lines, and at an oblique angle in the case of partially polarised lines.

Raman lines may be arranged in three chief groups [§] according to their widths : (1) lines of width less than 1 Å. (crystals) ; (2) lines of width 1 to 3 Å., which include most of the lines observed ; (3) bands of width 5 to 30 Å. (mineral compounds).

14. The Raman Effect in Gases and Vapours. The intensity of the light scattered from gases is very weak, but by the use of high pressures, spectrographs of great light-gathering power, and intense intrinsic illumination, the difficulties of investigation may be overcome.

Allen [||] has suggested that many of the faint lines in the secondary spectrum of hydrogen may arise from Raman scattering, the Balmer series lines acting as the exciting sources. Deodhar [¶] actually observed the Raman effect in the secondary spectrum, the frequencies of the Raman lines being shifted in some cases to the short wave-length side of the exciting lines, and in others to the long wave-length side.

---

[*] Depolarisation is the ratio of the intensity of the scattered radiation, relative to the vibrations parallel to the incident beam, to the intensity, relative to the vibrations perpendicular to this beam.

[†] *Trans. Farad. Soc.*, **29**, 813 (1929).

[‡] *Phil. Mag.*, **8**, 504 (1929).

[§] See Daure, *Ann. d. Physique*, **12**, 375 (1929).

[||] *Trans. Farad. Soc.*, **29**, 829 (1929).

[¶] *Zeits. f. Phys.*, **57**, 570 (1929).

Wood * has investigated dry HCl gas, excited by the mercury line, λ, 4,046 Å. The Raman line produced is one of wave-length 4,581·8 Å., and the frequency difference between the mercury line and this HCl line corresponds to a wave-length 3·466 μ in the infra-red, which is almost exactly the wave-length of the "missing line," or the centre of the gap between the two branches of the HCl absorption band.

Ammonia at atmospheric pressure gives a single line for each exciting line, carbon monoxide a line displaced by the frequency of its infra-red band, and carbon dioxide a line which is displaced by the difference in frequency of two infra-red bands.† Oxygen gives a pattern of equally spaced lines, and so does nitrogen and hydrogen.

McLennan ‡ carried out a series of experiments on the Raman effect with liquid-oxygen, nitrogen, hydrogen and nitrous oxide. His results indicated that with liquid-oxygen a mean vibration wave-number, of approximately 1,551·5 cm^{-1} was involved in the Raman effect, and a vibration of mean wave-number, approximately, 2.328·5 cm.$^{-1}$ with liquid-nitrogen. It is known that 1,554 cm.$^{-1}$ is indicated as the primary vibration wave-number of the oxygen molecule in its normal state. Hence the results would suggest that the primary vibration wave-numbers are the ones involved in the production of the four Raman lines observed.

Theory indicates that in liquid hydrogen there is one set of molecules in which the transitions of rotations from $m = 2$ to $m = 0$ can occur, and a second set in which the rotational transitions, $m = 3$ to $m = 1$, are possible. McLennan's results for liquid hydrogen show that :

(*a*) Some of the molecules are in the zero vibrational and zero rotational state.

(*b*) Others are in the zero vibrational and first quantum rotational states.

---

* *Phil. Mag.*, 7, 744 (1929).

† Rasetti, *Nature*, 123, 205 (1928).

‡ *Trans. Farad. Soc.*, 25, 797 (1929) ; *Roy. Soc. Canada, Trans.*, 24, 197 (1930).

No Raman effects were obtained corresponding to $m = 0 \rightarrow m = 1$, or $m = 1 \rightarrow m = 2$, rotational transitions.

The results also indicated that in liquid hydrogen there must be between two and three times as many molecules in the state (*b*) as compared with the number in the state (*a*), and thus support the view that hydrogen at low temperatures must be regarded as a mixture of two effectively distinct sets of molecules as described in Section 11.

Daure[*] has found that gaseous and liquid HCl give different Raman spectra, but it is impossible to explain this anomaly.

15. The Raman Effect in Liquids. An idea of the type of Raman spectra produced by liquids may be formed by inspecting Fig. 24 (*a*). An interesting feature with $C\,Cl_4$ is the triad of lines to the right of the exciting radiation, λ, 4,358 Å., and the equally-spaced triad to its left.

With very well purified water Dadieu and Kohlrausch[†] found two broad bands at about λ, 3 μ. Ganesan and Venkateswaran[‡] have shown that these bands from water at λ, 3 μ consist of three components, λ, 2·77 μ, 2·90 μ and 3·13 μ.

Solutions of salts in water give the Raman effect, the lines being characteristic of the salts and of water. Ganesan and Venkateswaran found that the well-known bands due to water in aqueous solutions of H_2SO_4, HCl and HNO_3 acids become sharper with increasing concentration of the acid. The similarities exhibited by solutions of carbonates of different metallic radicals, and the similarity of the sulphates and nitrates among each other, appear to support the view that the characteristic frequencies are those of the ionised acid radical. Rao[§] used HNO_3 at different concentrations and detected Raman lines due to the NO_3 ion, as well as lines which he attributed to HNO_3. On dilution, the NO_3 lines became more intense up to a maximum, after which they decreased in brightness, whereas the HNO_3 lines became progressively fainter and fainter, disappearing at that dilution at which the intensity of the NO_3 lines was a maximum.

---

[*] *Phil. Mag.*, 6, 1282 (1928).

[†] *Zeits. f. Phys.*, 60, 581 (1930).

[‡] *Indian Journ. Phys.*, 4, 195 (1929).

[§] *Nature*, 124, 762 (1929); see also Woodward, *Phys. Zeits.*, 32, 212, 261 (1931).

16. The Raman Effect in Solids. The case of gypsum, examined by Krishman,[*] is very interesting. The substance contains two molecules of water of crystallisation, and Krishman found, in addition to the wave-lengths which could reasonably be attributed to the SO_4 radical, three sharp lines at λ, $2{\cdot}8\ \mu$, $2{\cdot}9\ \mu$ and $3{\cdot}0\ \mu$. These are evidently due to the water of crystallisation and are practically in the same position as the components of the band observed with water and ice. Schæfer,[†] however, found only two lines due to crystal water. He suggests that the doublet, forming two of the three lines observed by Krishnan, can be interpreted as a coupling effect due to the association of water molecules.

The Raman lines obtained with crystals are sharp, becoming more diffuse with rise of temperature. In the case of substances not usually obtainable in large clear specimens, the Raman effect can be obtained by reflecting light from crystal surfaces. Menzies[‡] has used this method with potassium nitrate crystals.

Landsberg and Mandelstam[§] found that one of the Raman lines in the spectrum of Iceland spar corresponds to the optically inactive fundamental frequency of the CO_3 ion. Schæfer, Matossi and Aderhold[‖] have photographed the Raman spectra of YX_3 groups—carbonates, nitrates, chlorates and bromates—and of XY_4 groups—sulphates, selenates, ammonium phosphate and ammonium chloride. In the XY_3 groups the inactive frequency is always extremely strong, while the vibration parallel to the axis is always missing. In the XY_4 groups there are four frequencies, two of them inactive.

17. Theory of the Raman Effect. Raman suggested originally that the Raman lines were displaced by an energy amount equal to that required to raise a molecule from the normal state to some higher energy level, but if this were so, all Raman lines would correspond to infra-red absorption lines, and this is not the case.

Consider a light quantum, of frequency ν and energy $h\nu$, falling on a molecule in a given direction. The quantum and the molecule are to be regarded as a single system. This system has a number of other states of the same energy. Firstly, those in which the state of the molecule is unchanged, and the original quantum is scattered in a new direction without change of frequency; transitions to these states correspond to the classical scattering. Secondly, other states in which the state of the molecule is changed, its energy being altered by $\pm h\nu_1$, while a quantum of light of energy $h\nu \pm h\nu_1$ is scattered in some new direction. Changes to these states correspond to the Raman effect, and frequencies $\nu - \nu_1$ and $\nu + \nu_1$ are observed. The actual changes occurring in the molecule which give rise to these new frequencies can only be inferred from a detailed consideration of the possible modes of vibration of the molecule itself.

---

[*] *Indian Journ. Phys.*, **4**, 131 (1929).
[†] *Trans. Farad. Soc.*, **29**, 839 (1929).
[‡] *Loc. cit.*
[§] *Comptes Rendus*, **187**, 109 (1928).
[‖] *Zeits. f. Phys.*, **65**, 289 (1930).

The theory of the Raman effect was given, long before the experimental discovery of the phenomenon, in Kramers and Heisenberg's treatment * of dispersion from the point of view of the correspondence principle. In this theory some of the fundamental assumptions of the later-developed matrix mechanics † were already implied, so that the formula given by Kramers and Heisenberg for the electric moment of a system, perturbed by the field of a light wave, is exactly the same as it is when derived by the methods of wave mechanics.

It has been shown from the quantum theory that if we take an atom in the quantum state distinguished by the index k (which we will assume to be the normal state) the perturbation due to a light wave of frequency ν gives rise to harmonic components in the electric moment of the system having frequencies expressed by :

where l represents any other state of the system satisfying only the condition that the expression above must be positive, and ν_{lk} is the frequency corresponding to a transition of the scattering molecule from state k to state l, E representing energy. Considering the

---

* *Zeits. f. Phys.*, **31**, 681 (1925).

† See Klein, *Zeits. f. Phys.*, **41**
710 (1927).

c., *A*,

simplest case, in which the electric moment associated with the transitions involved in the process has the same direction, x say, as the electric vector of the light wave, the amplitude in the x direction of the harmonic component ν^*_{lk} in the electric moment is proportional to:

where the quantities x_{ls}, x_{ks} are the transition probabilities between the states l and s (in particular, if $x_{ls} = 0$, the corresponding transition is forbidden).

From this is appears that the condition for observing a transition (k l) as a Raman shift is not that this transition should occur in emission, or absorption (which means $x_{kl} \neq 0$), but that both the k and l states should combine with a third state s (or with more than one), in order to give at least one of the products $x_{ks}x_{ls}$, different from zero. This means that in an atom with a simple spectrum, such as that of any element in the first three columns of the periodic table, practically only forbidden transitions can take place in the Raman effect.

This reasoning also applies to the case of a diatomic molecule. Only, if the molecule is not polar, such as O_2 or N_2, transitions between the different vibrational states, without change in the electronic levels, do not give rise to radiation, because of the absence of an electric moment and, therefore, do not occur, although they are not properly " forbidden " transitions. Such transitions are expected to take place in the Raman effect, exactly as the " forbidden " transitions in atoms, because of the fact that different vibrational states, belonging to the same electronic level, combine with other states with a change in the electronic configuration. These considerations show that we have the possibility of deducing energy levels of molecules which cannot be detected in other ways.*

18. The Extreme Ultra-violet Region of the Spectrum. The extreme ultra-violet region of the spectrum may be arbitrarily defined as that part lying between wave-lengths 2,000 Å. and 150 A., the region between the latter limit and 10 Å. being described as belonging to soft X-rays.

---

* For a summary of the subject and an index bibliography, see Bhagavantum, *Indian Journ. Phys.*, 5, 237 (1930).

Schumann was the pioneer in this short wave-length work. He used a prism spectrograph of the usual form enclosed in an air-tight casing. The lenses and prisms were of fluorite, and he investigated the region λ, 2,000 Å.—λ, 1,200 Å.

The substitution of a concave grating for prisms and lenses of fluorite enabled workers, particularly Lyman, to push the limit of the spectrum considerably beyond the point reached by Schumann. The vacuum grating spectroscopes employed may be divided into two classes; in the first, the light falls nearly normally on the grating, in the second, grazing incidence is utilised. The great majority of instruments in use at the present time belong to the first type, but the second, which is becoming more common, will probably be used to a greater extent in the future. In practice, the vacuum inside the spectroscope should be as high as possible, and a special arrangement of pumps is necessary, whereby the gases from the neighbourhood of the source are removed at a point close to the slit. The use of a window between the source and the slit is, of course, debarred.

In the normal incidence type of instrument the concave grating, usually of about a metre radius, is placed at the end of a tube in a suitable holder; the other end of the tube carries the slit and photographic plate. In the best practice the only communication between the source of radiation and the body of the spectroscope is a short and narrow slit. If an electrical discharge is used as the source of radiation, the gas which flows in the neighbourhood of the discharge is removed on the grating side of the slit by a special pump connection.

In general, there are four types of radiation source, which have proved useful in the extreme ultra-violet, *viz.*, the hot spark, the spark operating in an atmosphere of transparent gas, the arc and the electrical discharge. With the hot spark arrangement the terminals are placed very close together, being separated by a distance of 1 mm., or less, and a disruptive discharge is applied, either directly, or indirectly, through an external gap, placed in series. This high-vacuum spark is rich in light of very short wavelength, and often gives out X-rays of sufficient penetrating power to reveal the bones of the hand.

For the study of absorption spectra Lyman * has shown that continuous radiation extending to λ, 900 Å. may be produced by charging a condenser of about one-half microfarad capacity with a direct current, and then discharging it through a vacuum tube of the internal capillary type, arranged in series with a half-centimetre gap. The absorbing substance is then introduced in front of the slit or, if it is a gas, some workers admit it to the body of the spectrograph.

Until fairly recently speculum was employed for the grating, but recently Wood succeeded in producing a satisfactory grating very lightly ruled on glass. This type is considered better than the speculum grating.

The arrangement of the various parts of a vacuum spectrograph may be considered by reference to that employed by Compton and Boyce,† and shown in Fig. 25. The source of light is at A, the grating at G, and the photographic plate at P. All are placed in an air-tight enclosure. The apparatus is opened to introduce, or remove, a photographic plate by removing the brass end plate E. The plate can be tilted through a small angle by means of an external control in which the rotation of the external magnet, M, causes the rotation of the armature on the inside of the spectroscope, and this action is transmitted through a set of small reducing gears to the pinion A′, which controls the tilt of the plate. The slit system, S, is specially designed to permit the maintenance of a large pressure ratio on its two sides, whereby an excellent vacuum is maintained in the main body of the spectrograph, although there is sufficient pressure of gas in the bulb B, containing the light source, to permit of suitable spectral excitation. To accomplish this the slit system is double. The first slit (the one nearest the light source) is the spectroscopic slit, and is adjusted to a width of about 0·001 cm. One centimetre behind it is a second slit, just enough wider to permit the unobstructed passage of the light from

---

* *Science*, **64**, 89 (1926).

† *Journ. Frank. Inst.*, **205**, 497 (1928).

the first slit to the entire surface of the grating, G. From between these two slits, gas is pumped away by a rapid diffusion pump at P_1. The gas which passes the second slit is pumped away from the main body of the spectrograph by another rapid diffusion pump P_4.

For the source of light, electrons from a Wehnelt cathode, C,

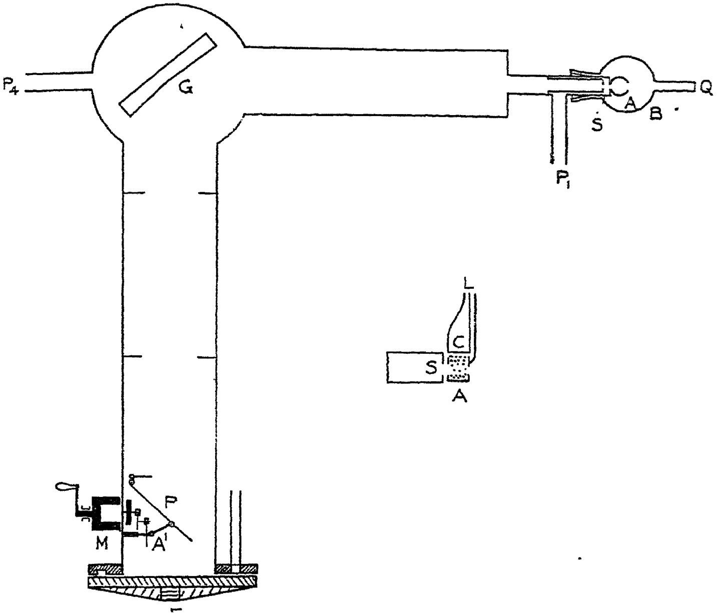


FIG. 25.—The vacuum spectrograph. (Compton and Boyce.)

are drawn through an applied potential difference to the anode, A. The space within the latter is field-free, and radiation is excited by electron impacts against the molecules. There are two openings at opposite sides of the box through one of which radiation passes to the slits, S, and from the other radiation is transmitted through a quartz window, Q, and enters a quartz spectrograph.

The shortest wave-length lines obtained with this arrangement were:

Helium	λ, 309·04 Å.
Neon	λ, 353·01 Å.

An example among the many used of the second type of spectrograph, where the radiation impinges on the grating at a large angle of incidence, is shown in Fig. 26, which represents the arrangement used by Hoag.* The source of light, slit, concave grating, and plate holder are all located on a circle, whose radius of curvature is one-half that of the grating. The image of the slit is then sharply focussed along the circle. This would be a typical Rowland mounting, if the slit were not so close to the grating, *i.e.*, if the angle of incidence were not so large. In designing the apparatus the usual equation:

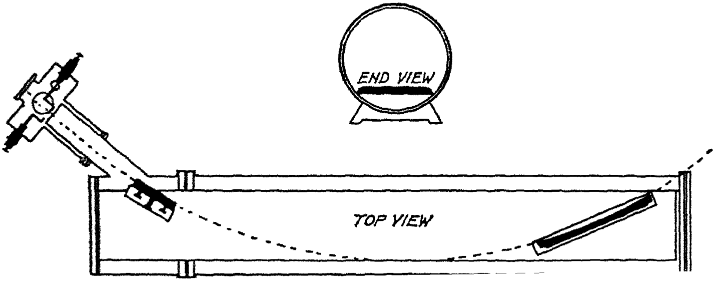


Fig. 26.—The vacuum spectrograph. (Hoag.)

$$n\lambda = d(\sin i - \sin \theta),$$

was used to compute the angle of diffraction, θ, for various values of the angle of incidence, i, approximately 80°. The dispersion of the instrument is very great, and with the hot spark as the source of radiation, spectra were photographed down to λ, 200 Å.

The published data for the extreme ultra violet are far too numerous to tabulate, and only a few of the results can be mentioned. Millikan,* using the hot spark as a source of radiation, photographed the region and determined wave-lengths down to 136·6 Å. in the case of aluminium, and to 149·5 Å. in the case of copper. He also photographed and located the L_α lines of Al, Mg and Na at λ, 144·3 Å., 232·2 Å. and 372·2 Å., respectively. By selecting certain strong lines in the spectra of the lighter elements, he endeavoured to show that the relations which connect frequency and atomic number in the X-ray region also hold in optical spectra. More recent investigations have indicated that his earlier identifications were not always correct.

Using a vacuum spectrometer for the extreme ultra-violet, designed by Siegbahn, Edlén and Ericson † succeeded in obtaining and measuring optical spectra down to λ, 100 Å. Regions up to λ, 1,250 Å. were measured with dispersions of 3·5 Å. per millimetre at λ, 100 Å. and 6·5 Å. per millimetre at λ, 1,000 Å., a concave grating on speculum metal with 571 lines per millimetre being used. In the case of copper, lines down to λ, 155·7 Å. were present as intense line groups, and the spectrum actually extended to λ, 126 Å. The measurements included about 140 lines below λ, 200 Å.

An investigation of the lighter elements from lithium to fluorine revealed hitherto unknown spectral series of highly ionised atoms. The lines reported by Millikan and Bowen ‡ were generally found within their limits of error. Edlén and Ericson were unable to obtain the lines at λ, 136·6 Å. and λ, 144·3 Å., ascribed by Millikan to oxygen, which had previously been considered as the shortest wave-lengths measured in optical spectra.

Edlén and Ericson also extended the ultra-violet region in the case of ionised beryllium to λ, 100·25 Å. Though the ratio of grating space to wave-length was about 180, the line appeared extremely sharp.

Söderman § recently measured the X-ray K-series of the lighter elements down to and including beryllium. The K_α line of this element, as given by Södermán, extends from λ, 111 Å. to λ, 122 Å. with its maximum at λ, 113·4 Å. It is interesting to note that the optical and X-ray spectra of the same element thus overlap.

---

* *Proc. Nat. Acad. Sci.*, **7**, 289 (1921).

† *Nature*, **124**, 688 (1929).

‡ *Phys. Rev.*, **23**, 1 (1924).

§ *Zeits. f. Phys.*, **52**, 795 (1929) ; *Phil. Mag.*, **10**, 600 (1930).

More recently Edlén * has extended the limit of optical spectra to λ, 40·28 Å. (a carbon V line). Other short wave-length lines measured include boron IV, λ, 52·68 Å., beryllium III, λ, 82·37 Å. The measurements also include lines of the series: boron IV, boron V, and carbon V, which are hydrogen- and helium-like spectra, the atoms having been stripped of their electrons.

Millikan and Bowen † have succeeded in showing that the law which connects the separation of regular X-ray doublets with atomic number holds for the lighter elements throughout the spectrum. They have demonstrated the applicability of a rule by which the position of irregular doublets may be predicted from element to element, a rule which had its origin in the study of X-rays. Finally, they have applied their investigations of series relations in general, and of the doublet laws in particular, to some of the basic principles of Bohr's atomic theory.

19. Ultra-violet Photomicrography. It is well known that the smallest distance, *d*, separating two points of an object is given by the relation :

$$d = \frac{\lambda}{2 \sin \alpha},$$

where λ is the wave-length of the light used in the medium surrounding the object, and α is the angle subtended at any point in the object by half the effective angular aperture of the objective. This equation is usually written :

$$d = {}_{2n \sin \alpha},$$

where λ_0 is the wave-length in vacuo, and *n*, the refractive index of the medium. It follows that the value of *d*, the distance between any two elements of recurring structure, is dependent on the wave-

---

Nature, **127**, 405 (1931).

† *Loc. cit*

length of the light used, and on the product $n \sin \alpha$, which is known as the numerical aperture (N.A.) of the illuminating and observing optical system.

The shortest wave-length that has sufficient luminosity in the visible spectrum for direct observation may be regarded as being in the region of wave-length 4,750 Å. By utilising ultra-violet radiations of a wave-length as short as λ, 2,200 Å., resolution will, other things being equal, thereby be doubled. The image cannot, of course, be a visual one, and the optical system must be composed of materials which are transparent to ultra-violet light. The immersion fluid must also be sufficiently transparent to ultra-violet light, and in this respect glycerine fulfils the purpose. The source of light is, as a rule, a high-tension spark discharge between metallic electrodes, usually magnesium, or cadmium. The necessary characteristics of the light are, that it should emit ultra-violet radiations in sufficient quantity, and that its spectrum should mainly consist of a few intense bright lines or groups of lines.

Mees * has suggested that the mercury line λ, 3,650 Å. is particularly suited for photomicrography. The theoretical limit of its resolving power with an objective of N.A. = 1·4 is 0·13 μ. As a spectral line, it not only meets the specifications for ideal illumination, but, if obtained from a high-pressure mercury arc, is one of the most intense sources of monochromatic energy in the ultra-violet. Its greatest advantage, however, lies in the fact that a glass system can be used. Mees has pointed out that with λ, 2,750 Å. radiation the only objective available has an N.A. = 1·25, which gives a theoretical resolving power of 0·11 μ. The difference between the resolution of 0·13 and 0·11 hardly seems sufficient justification to make the whole optical system of quartz with a complicated light source, such as the condensed magnesium spark. Selective absorption, which proteins show for λ, 3,650 Å., makes the arrangement valuable. Cedar oil possesses a high absorption for λ, 3,650 Å. and the best transmitting oil for this wave-length is sandalwood.

---

* *Journ. Frank. Inst.*, **210**, 525 (1926). See also Trivelli and Foster, *Journ. Opt. Soc. Amer.*, **21**, 124 (1931).

20. The Measurement of X-ray Wave-lengths. In general, long X-ray wave-lengths have been measured by four methods, using

(*a*) crystals with large spacings,
(*b*) ruled gratings,
(*c*) the photo-electric effect,
(*d*) the calorimeter method.

(*a*) The first reliable value of the wave-length of X-rays was obtained by Bragg.* He determined the atomic arrangement in a rock-salt crystal, and used the calculated distance between its layers of atoms as a standard for measuring the wave-length of the palladium K line from the formula :

$$\mathrm{n}\lambda = 2d \sin \theta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where n is the order of the spectrum, d, the spacing between the atomic planes, and θ, the glancing angle. A narrow pencil of X-rays, defined by a system of slits, is allowed to fall upon a crystal face. The reflected ray is received in an ionisation chamber, and the angle θ determined. De Broglie † introduced a photographic method whereby the whole spectrum was recorded on a photographic plate by rotation, to and fro, of the crystal.

When one takes into account the refractive index, n, of the crystal for X-rays, the above relation becomes :

$$\mathrm{n}\lambda = 2d \sin \theta \Big(1 - \frac{}{\sin^2\theta} \qquad (9)$$

Now the grating constant of a crystal whose structure is known can be calculated in terms of Avogadro's constant. Thus, for a simple cube crystal :

$$d = \Big(\frac{W}{} \qquad (10)$$

where W is the molecular weight of the substance, N, the number of molecules per gram-molecule, and ρ, the crystal density. The chief uncertainty in the expression for the grating space would seem to be that due to the uncertainty in Avogadro's number. This is estimated by Millikan to about 1 part in 1,000, which means an uncertainty in the value of d, and hence also in the value of the wave-length, λ, of 1 in 3,000.

---

* *Proc. Roy. Soc.*, 89, 248 (1913).

† Les Rayons X.

The determination of the structure of rock-salt was the starting point of all measurements of wave-lengths and spacings. Rock-salt, however, is not well suited for very accurate comparisons. The crystal is generally ill-made, consisting of a mass of smaller crystals, imperfectly aligned with each other. Calcite is much better formed, and is now in general use as the standard of measurement.

When measuring the wave-length of soft X-rays, or those of long wave-length, crystals of large interatomic spacings must be used, and owing to the absorption of these rays, which are generally of weak intensity, it is necessary to employ a vacuum spectrograph. Among the earlier known crystals, gypsum, mica and sugar are the only ones that can be used for reflecting the long wave-lengths, and the upper limit that can be measured with these is λ. 18 A. There are, however, many organic compounds suitable for this purpose. Especially lauric acid and palmitic acid have proved to be useful. Their reflecting power is good, and their melting-points so high that they do not appreciably evaporate in vacuum. In practice, the acid is allowed to solidify upon a plate and the molecules, as the X-ray analysis shows, gather themselves together in an ordered fashion, forming thin sheets, in which the molecules lie side by side and transversely to the sheets. A plate carrying a thin layer of the substance is mounted on the X-ray camera, so that the plane surface contains the axis of rotation, and the plate is oscillated through a few degrees about the position of reflection. The incident monochromatic rays are defined by slits which are parallel to the axis of the instrument. and the crystal in this case is to be considered as consisting of a number of mono-molecular layers, in each of which the molecules are parallel to each other and transverse to the layer.

The high-vacuum spectrograph, as used by Thoraeus and Siegbahn,* was in direct communication with a Coolidge tube, and a crystal of palmitic acid was employed. Thoraeus † continued this work, and Dauvillier * used a crystal of a fatty acid, *e.g.*, melissic acid on lead. He traced the K_a line of carbon in the third order spectrum, corresponding to λ, 138 Å. Other measurements have been made by Zumstein † and van der Tuuk. ‡

---

* *Ark. f. Mat. Astron. och Fysik., Stockholm*, **19**, 12 (1925).

† *Phil. Mag.*, **1**, 312 (1926) ; **2**, 1007 (1926).

(*b*) Compton and Doan § secured X-ray spectra from a diffraction grating ruled on speculum metal, the X-rays striking the reflecting surface at a sufficiently sharp glancing angle, within the critical angle for total reflection. Within this critical angle, which in their experiments, with wave-lengths smaller than 1·6 Å., was less than 25′ of arc, the diffraction grating may be used in the same manner as in optical work. The wave-length is given by the usual formula :

$$\mathrm{n}\lambda = d\,(\sin i - \sin r),$$

where i is the angle of incidence, r, the angle of diffraction, n, the order, and d, the grating space. For small glancing angles, this may be more conveniently written as,

$$\mathrm{n}\lambda = d\,(\cos\theta - \cos\{\theta + a\}),$$

in which θ is the glancing angle and a, the angle between the zero and nth order of spectra. For the small angles employed, this equation approximates to

n

The principle involved in the method is illustrated in Fig. 27. If X-rays which have passed through slits, S_1, S_2, fall on the surface of the grating, G, at a glancing angle, θ, which is within the angle of total reflection for the radiation under consideration, the totally reflected X-rays will strike the plate, P, at R, and the radiation, diffracted by the grating, at a point S. D is the portion of the direct beam which is used as a reference line. The grating space was large, $d = 2{\cdot}000 \times 10^{-3}$ cm.

Wadlund ‖ further extended the method. He found that with small glancing angles it was necessary to expand equation (11) to a more accurate form so as to include fourth-degree terms, *viz.*:

---

* *Comptes Rendus*, **182**, 1083 (1926) ; **183**, 193 (1926).

† *Phys. Rev.*, **25**, 747 (1925).

‡ *Zeits. f. Phys.*, **41**, 326 (1927).

§ *Proc. Nat. Acad. Sci.*, **11**, 598 (1925).

‖ *Phys. Rev.*, **32**, 841 (1928).

$$n\lambda = d\,(\alpha\theta + \tfrac{1}{2}\alpha^2 - \text{4th degree terms}).$$

Thibaud * used glass-ruled gratings under very high glancing angle, nearly 90°, in a vacuum spectrograph. The grating constant in one case was $d = 8{,}477$ Å. units, and the diffracting part of the grating surface was reduced to a width of 1 mm. by two collodion films deposited on the surface. The geometrical origin of the beam is therefore readily determined. All the linear and angular constants required for calculation are found by recording the same spectrum at two different positions of the plate, separated by a known distance.

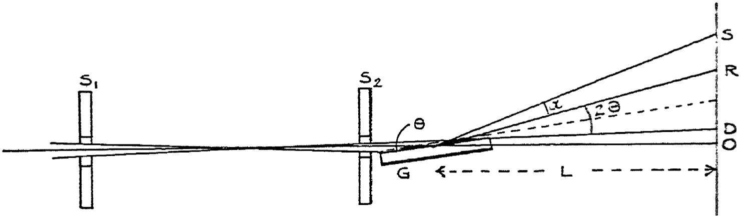


FIG. 27.—Measurement of the wave-length of X-rays by means of a grating.

Thibaud noted that even lines of long wave-length remain tolerably narrow, and he attributes the widening of the lines when the wave-length increases, as noted by Thoraeus † and Dauvillier, ‡ to the crystal grating they used; in part, because on account of the high absorption coefficient, the number of reflecting planes effective in the diffraction is small, and in part because of the refraction effect. Ewald has computed that in a crystal of refractive index n the diffracted lines show an angular where $\delta = (1 - n)$. This would lead to a width of 7 Å. for a line at λ, 68 Å. with a "fatty acid grating" of index $\delta = 10^{-2}$. The predicted value agrees with the widening observed experimentally.

---

* *Comptes Rendus*, 182, 55 (1926); *Journ. Opt. Soc. Amer.*, 17, 145 (1928); *Journ. de Phys.*, 1, 37 (1930).

† *Loc. cit.*

‡ *Journ. de Phys.*, 8, 1 (1927).

The effect of the refractive index is thus a serious difficulty in the extension of crystal methods to the longer wave-lengths. Such difficulties are obviated by the use of the ruled grating at glancing incidence.

Hunt [*] determined the K_α line of C to be 46·0 Å. by means of a vacuum X-ray spectrograph and Osgood,[†] using a two-metre concave glass grating with 800 lines per millimetre, noted a line, which he ascribes to iron, at λ, 215 Å. Bearden [‡] employed the K lines of Cu with a glass grating of 600 lines per millimetre, and also with a glass and speculum-metal grating, each with 50 lines per millimetre. The values of the wave-lengths obtained were :

$$K_\alpha = 1{\cdot}5422 \pm 0{\cdot}0002 \text{ Å.}$$
$$K_\beta = 1{\cdot}3926 \pm 0{\cdot}0002 \text{ Å.}$$

Cork [§] worked with plane-ruled gratings having 30,000 and 14,000 lines per inch, respectively, photographing the L series lines of Mo. The wave-lengths for L_α and L_β, as given by Siegbahn using a gypsum crystal, are 5·3943 Å. and 5·1658 Å., respectively. If a calcite crystal were employed, and approximate correction made for refraction, wave-lengths of 5·3960 Å. and 5·1674 Å. should result, whereas the average of the grating measurements in Cork's experiments gave λ, 5·4116 Å. and λ, 5·1832 Å. Cork suggests that the discrepancies are due to anomalous variation of the refractive index of the crystal.

Howe [‖] has examined several lines in the L-series, and the K_α line of carbon, the wave-length of the latter being 44·60 ± 0·04 Å. Kellström [¶] has also measured the L-series lines of the elements Cu — Ca, referred to the K_α line of Al, the wave-length of which has been determined by crystal precision measurement. Söderman,* using different gratings, has measured the K lines of Al, Mg, Na, F, O, N, C, B and Be. His lowest recorded wave-length is that for the K_β line of Al, *viz.*, 7·952 Å., and his greatest wave-length that of the K_α line of Be, *viz.*, 115·7 ± 0·15 Å. Other measurements include the K_α line of B, 67·71 Å., and the K_α line of C, 44·54 Å.

---

[*] *Phys. Rev.*, **30**, 227 (1927).

[†] *Ibid.*, **30**, 567 (1927).

[‡] *Proc. Nat. Acad. Sci.*, **15**, 528 (1929).

[§] *Phys. Rev.*, **35**, 1456 (1930).

[‖] *Ibid.*, **35**, 717 (1930).

[¶] *Zeits. f. Phys.*, **52**, 795 (1929).

(*c*) The photo-electric method of determining the wave-lengths of very long X-rays measures, by means of a retarding potential, the energies of photo-electrons ejected by soft X-rays, and translates the maximum energies into wave-lengths by means of the quantum relations. The results obtained by various experimenters seem to be quite consistent for each worker, but vary somewhat from worker to worker. The method offers an indirect means of measuring the wave-length, and by means of it the gap separating the X-ray region and the ultra-violet region of the spectrum may be said to have been closed some years ago. But investigations of this type involve so many difficulties and uncertainties that the results obtained by them cannot be regarded as entirely conclusive.

Richardson and Bazzoni † showed that it was possible to detect the excitation of characteristic soft X-rays, such as the K X-rays of carbon, by this photo-electric method. The substance under investigation was bombarded with electrons in a highly-evacuated quartz bulb, and the radiation thus generated, after passing between two parallel plates of a vacuum condenser to filter out ions and electrons, was received on a metal plate from which the photo-electric emission could be measured. The photo-electric current increases with the thermionic electron current, and with the potential difference driving the latter. If the quotient of the photo-electric current and the thermionic current is plotted against this potential difference, the excitation of characteristic X-rays setting in at certain voltages could be detected from the existence of discontinuous changes of slope in the curves thus obtained. Similar observations were made almost simultaneously by Hughes,* by means of the apparatus shown in Fig. 28. The radiation was produced by the impact of electrons from a hot tungsten filament, F, on a carbon, or boron, target, T. Part of the radiation fell on the silver plate Z, which emitted photo-electrons under the action of the radiation. The photoelectric current was measured by the rate of charging up of an electrometer.

---

* *Phil. Mag.*, **10**, 600 (1930); *Zeits. f. Phys.*, **65**, 656 (1930).
† *Ibid.*, **42**, 1015 (1921).

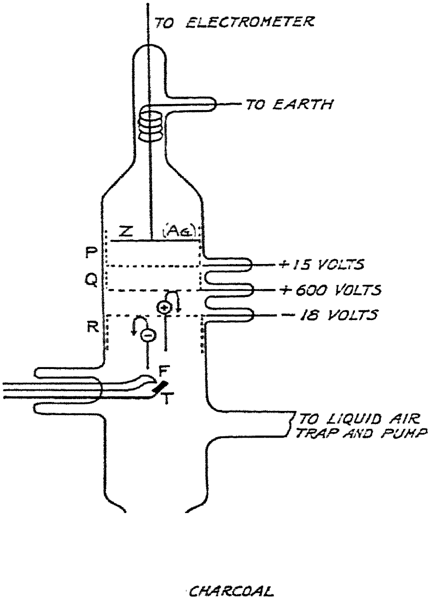


Fig. 28.—Detection of soft X-rays.

As the photo-electric current rarely exceeded 10^{-13} amp., and as the electron current from F to T was generally between 10^{-5} and 10^{-3} amp., it was necessary to ensure that the effect measured was really due to the photo-electric effect of the radiation, and not in some way to electrons, or positive ions, finding a path upwards. To protect against this, fine gauzes were fitted into the apparatus, as shown. The field accelerating the electrons from F to T was produced by keeping F at zero potential, while the potential of T was varied from + 5 to + 500 volts. Thus, if the lower gauze, R, was maintained at a negative potential, no electrons could possibly pass upwards from the neighbourhood of the hot cathode and target; but, on the other hand, this arrangement would help positive ions, if any were produced, to pass through the gauze, R. To turn these back, the gauze, Q, was kept at a higher potential than any value of that applied to F. Hence the positive ions, if any came through R, would be turned back towards R. The only way then for the metal plate Z to acquire a positive charge would be for the few positive ions, turned back on R, to release electrons therefrom, and for these electrons, by virtue of R being 18 volts negative to Z, to travel to Z. This, however, would give Z a negative charge. A wide-mesh gauze, P, was introduced between Q and Z to increase the steadiness of the electrometer needle. The total photo-electric current leaving the metal plate Z was measured as a function of the energy of the impinging electrons. A discontinuity in the slope of the curve was taken to indicate the excitation of the characteristic radiation. The wave-length of the radiation is connected with the energy of the electrons by the well-known quantum relation:

---

* *Phil. Mag.*, **43**, 145 (1922).

$$\mathbf{V}\mathbf{e} = h\nu = \frac{hc}{\lambda},$$

where **V** is the potential accelerating the electrons, **e**, the charge on the electron, *h*, Planck's constant, ν and λ, the frequency and wave-length, respectively, of the radiation, and *c*, the velocity of light. When **V** is expressed in volts and λ in Å. units we have:

$$\mathbf{V} = \frac{12{,}331}{\lambda}.$$

Curves representing the variations of photo-electric current with accelerating potential, obtained by McLennan and Clarke * for boron and beryllium, are shown in Fig. 29. These, it will be seen, exhibit discontinuities at 148 volts, and at 78·0 and 89·0 volts, respectively. The discontinuities approximate to wave-lengths, 83·6 Å., and the range—λ, 157·6 Å. to λ, 118·2 Å.—respectively.

Many measurements have been made by different workers using the photo-electric emission method, and recently Richardson and his co-workers * have examined the excitation of soft X-rays from single crystal surfaces of graphite, aluminium, and nickel. The results obtained with these single crystals as against polycrystalline surfaces indicate that the simpler the crystal structure of the surface the fewer the number of critical potentials. Thus in the case of experiments on the (100) face of a single nickel crystal, in the range 1 to 30 volts, only two discontinuities were observed, indicating that the more numerous breaks obtained with the polycrystalline surface are due to reflection, or diffraction, from the various crystal faces of different orientations. The critical potentials may be arranged in groups having the same type of numerical relationships as the frequencies of lines in a set of bands.

---

* *Proc. Roy. Soc., A*, **102**, 391 (1923).

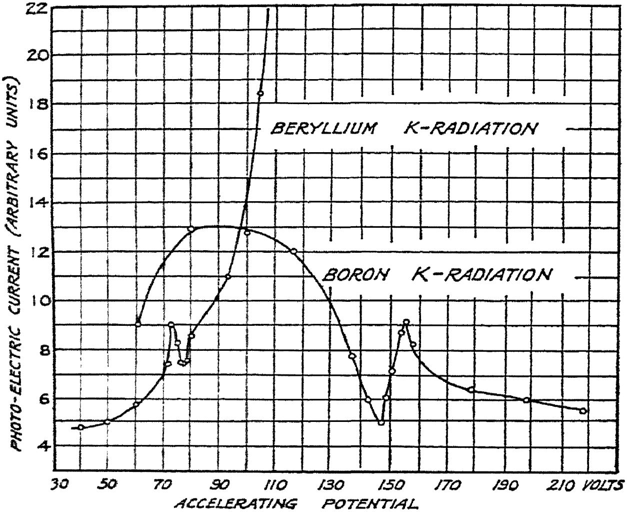


FIG. 29.—Detection of critical potentials of soft X-rays.

(*d*) Another method of determining the wave-lengths of X-rays has been introduced into X-ray spectroscopy by Ham.* The material to be investigated is made the target of a water-cooled Coolidge X-ray tube, and the heat generated at the target is compared with the electrical energy imput into the tube, for various retarding potentials between the anode and the glass walls of the tube. This makes it possible to plot, for any tube voltage, the ratio of the number of incident electrons from the cathode stream to the number of secondary electrons, emitted from the target, as a function of the velocities of the secondary electrons. This ratio suddenly increases when the tube potential is made to exceed one of the critical potentials of the anode material. In this way a flow-calorimeter is made to act as a spectrometer, in which wave-lengths are given from absolute energy measurements by means of the quantum relation.

---

* *Proc. Roy. Soc.*, **128**, 1

21. Determination of the Values of Physical Constants. The discovery that X-rays may be diffracted by crystals was one of the utmost significance. Not only did this discovery show the identical character of X-rays and light, which had previously been questioned, but it also afforded a means which has made it possible to examine the interior structure of matter with a remarkable definiteness. By the help of this discovery W. H. and W. L. Bragg † analysed the atomic structure of crystals. Moseley ‡ studied the spectra of X-rays, finding from the beautiful regularity of the changes in the spectra, as we pass from one element to the next, that each element has in its structure one more electron than that of the element next lighter. The measurement of X-ray wave-lengths has supplied us with what is perhaps our most precise method of determining Planck's constant h, which plays so important a part in the photo-electric effect, and is fundamental in the quantum theory. In fact, it is difficult to find an aspect of atomic, or molecular, structure which has not been affected by the consequences of Laue's discovery of the diffraction of X-rays.

Closely associated with the measurement of the wave-length of

---

* *Bull. Amer. Phys. Soc.*, **2**, 12 (1927).

† See "X-rays and Crystal Structure."

‡ *Phil. Mag.*, **27**, 703 (1914).

X-rays, and the analysis of the structure of crystals, is the counting of the number of molecules in a cubic centimetre of the crystal. Such a measurement affords us, likewise, a knowledge of Avogadro's number and the electrical charge on the electron. One finds values for these constants which differ by a surprisingly large amount from the accepted values.

Using the value of the wave-length of the copper K_β line, as found by Bearden, the grating space d of a calcite crystal can be obtained from equation (9). Siegbahn and Dolejsek * found for θ in this case a value $12^\circ\ 15'\ 28{\cdot}2''$ for $n = 1$ with the crystal at 18° C., whence $\sin\theta = 0{\cdot}229334$. Compton † calculated the value of $(1 - n)/\sin^2\theta$ for calcite (100) planes and from these results:

$$d \text{ (calcite)} = 3{\cdot}0366 \pm 0{\cdot}0004 \text{ Å. } (18^\circ \text{ C.}).$$
$$d \text{ (calcite)} = 3{\cdot}0367 \pm 0{\cdot}0004 \text{ Å. } (20^\circ \text{ C.}).$$

From a relation similar to equation (10) we find for Avogadro's number:

$$N = \frac{\mathbf{n}M}{\rho\phi} \cdot \frac{1}{d^3},$$

where for calcite $\mathbf{n} = \frac{1}{2}$,

$$\rho = 2{\cdot}7102 \pm 0{\cdot}0004 \text{ gm. per c.c.,}\ddagger$$
$$M = 100{\cdot}078 \pm 0{\cdot}006, \S$$
$$\phi = 1{\cdot}09630 \pm 0{\cdot}00007, \|$$
$$d = 3{\cdot}0367 \pm 0{\cdot}0004 \times 10^{-8} \text{ cm.}$$

Thus $N = 6{\cdot}0142 \pm 0{\cdot}0026 \times 10^{23}$ molecules per gram-molecule.

Knowing Avogadro's constant, the electronic charge, **e**, is given in terms of Faraday's constant of electrolysis (the faraday) F,

Now $F = 9648{\cdot}9 \pm 0{\cdot}7$ electromagnetic units, and c, the velocity of light $= 2{\cdot}99796 \times 10^{10}$ cm. per sec. so that,

$$\mathbf{e} = 4{\cdot}810 \pm 0{\cdot}002 \times 10^{-10} \text{ electrostatic units.}$$

---

* *Zeits. f. Phys.*, 10, 160 (1922).

† "X-rays and Electrons," p. 212 (1926).

‡ See Defoe and Compton, *Phys. Rev.*, 25, 618 (1925).

§ See Birge, *Phys. Rev. Supp.*, 1, (1929).

‖ See Beetz, *Phys. Rev.*, 25, 621 (1925).

The most direct method of obtaining a value of Planck's constant h, on the basis of this work is through the measurements of the limit of X-ray spectra by Duane, and his collaborators. Writing the Duane-Hunt [*] law in the form :

$$h = \frac{\mathbf{Ve}\lambda}{}$$

where $\mathbf{V}$ is the potential applied to the X-ray tube, and λ, the minimum wave-length of the emitted X-rays, and expressing λ by means of equation (9), remembering that for this experiment $n = 1$, we have :

$$h = \frac{2}{c}\mathbf{Ve}d \sin\theta\,(1 - b),$$

where $$b = (1 - n)/\sin^2\theta = 1{\cdot}46 \times 10^{-4}.$$

The experiments of Duane, Palmer and Chi-Sun-Yeh [†] give directly the value of $\mathbf{V}\sin\theta = 2039{\cdot}9 \pm 0{\cdot}9$ volts. Using the values of $\mathbf{e}$ and d obtained above, we thus get :

$$h = 6{\cdot}629 \pm 0{\cdot}004 \times 10^{-27} \text{ erg. sec.}$$

If we write Bohr's expression for the Rydberg constant, $\mathbf{R}$, in the form :

$$\mathbf{R} =$$

we may solve for $\frac{\mathbf{e}}{m}$. Using the value, $\mathbf{R} = 3{\cdot}28988 \times 10^{15}$ [‡] we thus find :

$$\frac{}{m} = 1{\cdot}769 \pm 0{\cdot}003 \times 10^{7} \text{ electromagnetic units per gm.}$$

A comparison of the values, thus obtained, with the accepted values found by other methods, and summarised by Birge, [§] is shown on p. 208.

The most significant differences are in the values of $\mathbf{e}$ and of $\mathbf{e}/m$, since these quantities are subjected to independent experimental

---

[*] *Phys. Rev.*, **6**, 166 (1917).
[†] *Journ. Opt. Soc. Amer.*, **5**, 376 (1921).
[‡] *Proc. Roy. Soc., A*, **122**, 358 (1929).
[§] *Loc. cit.*

	Calculated from Bearden's Value for λ.	Accepted Value.	Percentage Difference.
d (calcite) .	3·0367 A°	3·0283 Å	0·3
N . .	$6{\cdot}014 \times 10^{23}$	$6{\cdot}064 \times 10^{23}$	0·8
$\mathbf{e}$ . .	$4{\cdot}810 \times 10^{-10}$	$4{\cdot}770 \times 10^{-10}$	0·8
h . .	$6{\cdot}629 \times 10^{-27}$	$6{\cdot}547 \times 10^{-27}$	1·2
$\mathbf{e}/m$ . .	$1{\cdot}769 \times 10^{7}$	$1{\cdot}769 \times 10^{7}$ (deflection)	0
		$1{\cdot}761 \times 10^{7}$ (spectrum)	0·5

measurement. It is interesting to note that if one uses these new values of $\mathbf{e}$ and h, better agreement is found with Eddington's recent speculation * regarding Sommerfeld's constant α. He has brought forward reasons for believing that $1/\alpha$ should be 136 where $\alpha = 2\pi\mathbf{e}^2/hc$. Using the accepted values of $\mathbf{e}$, h and c, $1/\alpha = 137{\cdot}2$. The values above give $1/\alpha = 136{\cdot}45 \pm 0{\cdot}15$. It is difficult to find the sources of error. The correction introduced for refraction has been verified by several workers. Avogadro's number involves no additional uncertainty, except that of crystal density. The existence of crystal faults is well known, and Joffe † and Zwicky, ‡ among others, have emphasised the existence of resulting gaps in crystal lattices. From this it follows that minute crystal elements should have a higher density than the large-scale crystals. Such a difference is in the wrong direction to account for the difference between " crystal " and " ruled grating " wavelengths. The difference is nearly the same whether a comparatively perfect crystal, such as calcite is used, or whether one employs the relatively imperfect crystal, rock-salt.

This directly conflicting experimental evidence regarding these fundamental constants is not a new probelm. Thus, for example, there is the outstanding difference in the value of $\frac{\mathbf{e}}{m}$, determined by deflection experiments, as compared with that resulting from spectroscopic observations.

---

* *Proc. Roy. Soc.*, *A*, **126**, **696** (**1930**) ; Cambridge, *Phil. Soc. Proc.*, **27**, **15** (1931).

Zeits. f. Phys., **62**, **730** (**1930**).

Nat. Acad. Sci. Proc., **15**, **253** (**1929**).

22. The Refraction of X-rays. According to Bragg's law for the reflection of X-rays from crystal planes,

$$\frac{\lambda}{2d} : : \frac{\sin\theta}{\mathrm{n}},$$

should be a constant for all orders of reflection, but refinements in the measurement of the wave-length soon showed that this ratio was not quite constant. The departure from constancy was attributed by Stenström * to a slight refraction of the rays on entering and leaving the crystal surface. Darwin † had previously predicted the probable existence of such deviations from theoretical considerations. In his treatment of the general problem of reflection he assumed the X-ray phenomena to constitute a branch of optics, and proceeded to build up an expression for the intensity of reflection on the basis of the electromagnetic theory. He recognised, however, that the part played by the emission of high-speed electrons in the absorption of X-rays presents an important difficulty to his method. A second assumption, apparently necessary, is that the amplitude of the wave passing through matter diminishes exponentially, with an absorption coefficient equal to half that found for the intensity. In this connection Darwin pointed out that although the absorption of a homogeneous beam is believed to be exponential, the process is probably a statistical one. In some respects, therefore, the second assumption is less satisfactory than the first. But his result, relative to the failure of Bragg's law, has now been verified. As a corollary to his theory of reflection, Darwin found the relation :

$$\theta - \theta_0 = -\,\delta \operatorname{cosec}\theta \sec\theta,$$

where θ is the grazing angle of incidence, θ_0, the angle of reflection (experimental) and $\delta = 1 - n$, n being the refractive index of the substance. Hence the corrected form of Bragg's law is, as stated previously,

$$\mathrm{n}\,\lambda = 2d\sin\theta\left\{1 - \frac{\delta}{\sin^2\theta}\right\}.$$

---

* "Dissertation," 1919.

† *Phil. Mag.*, 27, 320 (1914).

Now if the rays make an angle θ_1 with the surface at entrance and θ_0 after entrance, then since the molecular planes are supposed parallel to the surface, the refraction is given by :

$$n = \frac{\cos\theta_1}{\cos\theta_0}.$$

The true wave-length is represented by $n\lambda = 2d\sin\theta_0$, while θ_1 is the angle actually measured. The departure of n from unity is δ, where $\delta = 1 - n = 1 - \frac{\cos\theta_1}{\cos\theta_0}$. For spectral orders m and n this may be written * :

$$\delta = \frac{\left(\frac{\sin\theta_m}{\mathrm{m}}\right)^2 - \left(\frac{\sin\theta_n}{\mathrm{n}}\right)^2}{} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The actual values of the wave-length as determined by Stenström by means of a photographic method, for various orders, were qualitative in that they showed a progressive change with order. Stenström's interpretation of his results was criticised by Knipping † who claimed that the special arrangement of the atoms of the crystals can be adjusted to explain such differences. Subsequently, Duane and Patterson ‡ and Siegbahn § observed the effect with X-rays of medium wave-length in the lower orders. Hjalmar, ‖ using a photographic method and various wave-lengths, investigated the reflection from crystalline surfaces up to the tenth order. Davis and Terrill,¶ by means of the ionisation spectrometer method, were not able to determine δ within 100 per cent. of the correct value. This refractive effect is very small. For example, the bending of the molybdenum K_α radiation entering a calcite crystal at the proper angle for reflection is about 3 seconds of arc, which is near the limit of measurement. This small refrac-

---

* See Stenström, *loc. cit.*

† *Zeits. f. Phys.*, 1, 40 (1920).

‡ *Phys. Rev.* 16, 532 (1920).

§ *Comptes Rendus*, 174, 745 (1922).

‖ *Zeits. f. Phys.*, 15, 63 (1923).

¶ *Proc. Nat. Acad. Sci.*, 8, 357 (1922).

tive bending can be greatly increased by cutting the surface of the crystal at an angle ϕ to the reflecting planes.* The crystal is so cut that, as the ray enters the crystal at the proper angle for reflection from the planes, it makes a very small angle with the surface (see Fig. 30). The bending at the surface is greatly increased by this device.

For the purpose of accurate measurement of the wave-length the crystal is turned through an angle $\beta = (180^\circ - 2\theta)$ where θ is the glancing angle. The experiments were first performed with the natural (100) face of a very perfect crystal of pyrites. The crystal was ground and polished, so that the surface made an angle $\phi = 6^\circ\, 31'\, 57{\cdot}5''$ with the reflecting planes. The position of the crystal and path of rays is shown in Fig. 30, (A). The crystal was then turned through an angle $\beta = (180 - 2\theta)$ at which reflection was then observed (position B). It can be shown that θ may be expressed in terms of the first order readings by the equation :

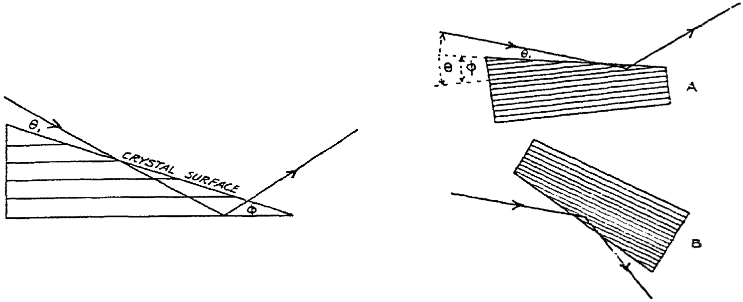


FIG. 30.—Refraction of X-rays.

$$\delta = \frac{(\sin\theta - \sin\theta_0)(\sin^2\theta - \sin^2\phi)}{\sin\theta\cos^2\theta} \qquad (13)$$

where $\theta = \frac{1}{2}(180^\circ - \beta$ and θ_0 is the true angle that the rays make with the crystal plane inside the crystal.

The true value of θ_0 was found by approximations. The value of δ, obtained for the uncut crystal by means of equation (12), was used in the equation :

---

* See Davis and Hatley, *Phys. Rev.*, **23**, 290 (1924); Davis and von Nardroff, *Proc. Nat. Acad. Sci.*, **10**, 60 (1924).

$$n = \frac{\cos}{\cos(\theta_0 - \bar{\phi})} \quad . \quad . \quad . \quad . \quad . \quad .$$

to obtain a tentative value of θ_0. The latter was then used in equation (13), together with the measured values of θ and ϕ, to

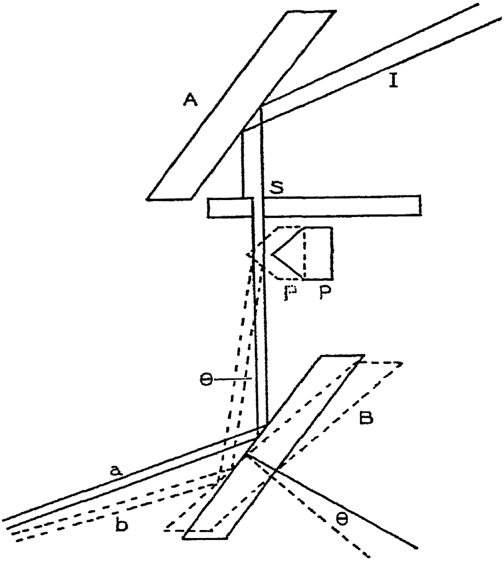


FIG. 31.—Refraction of X-rays by a prism.

calculate an approximate value of δ. The latter value of δ was again used in equation (14) to calculate a more accurate value of θ_0, *etc.*

Since X-rays are actually refracted, it should be possible, by sufficient refinement of apparatus, to measure the bending on passing through a prism, as in the case of light. This has been done by Larrson, Siegbahn and Waller.* The refractive effect was made as large as possible by using a prism of very large angle. The beam of X-rays passed over and through the extreme obtuse point of the prism, and then fell upon a photographic plate. One part of the beam was refracted and the other part totally reflected. The results obtained by this method confirm those by the cut crystal method, but are possibly not quite so accurate. The method is subject to the limitation that the refracting edge must be ground with great accuracy.

---

* *Naturwiss.*, 52, 1212 (1924).

A method of measuring the minute bending of X-rays has also been devised by Davis and Slack,* using a special type of X-ray spectrometer. Two crystals are arranged as shown in Fig. 31. The narrow beam, I, of incident X-rays is reflected from the crystal (calcite) A, through a limiting slit, S, to a crystal (calcite) B, and from B to an ionisation chamber. The crystal B is mounted in such a way that it can be turned through any small angle, as desired. The beam reflected into the ionisation chamber is denoted by a. If, now, crystal B is rocked through a very small angle each side of its maximum reflection position, very sharp curves are obtained which are known as "rocking curves." These curves are very narrow and one such curve is shown by the full line of Fig. 32. The prism P, in which the refraction is to be measured, is mounted on a carriage, so that it may be run in and out of the path of the X-ray beam. When the prism is in the path of the beam, the ray is refracted through an angle θ. Crystal B is now rotated to reflect this refracted beam, and a new "rocking curve" is obtained, as shown in the dotted curve. The angular distance between the peaks of the two curves is equal to the angle of refraction.

Another interesting prism method of measuring n has been devised by Stauss.† His experimental arrangement is shown in Fig. 33. Radiation from the slit, S, fell upon the prism P, which had its refracting edge, A, over the centre of rotation of a spectrometer. Slightly to the front and to the side of the prism was a lead block, B, which together with the prism acted as a kind of slit. The primary beam was defined by A and B and refraction occurred

ys. Rev., **27**, 18 (1926).
Ibid., **36**, 1101 (1930).

in the neighbourhood of A. After the primary and refracted beams were registered on the photographic plate, M, the prism was rotated through a small angle, ϕ, to the position (*b*), and the beam was then totally reflected from the face AA′ at the angle β.

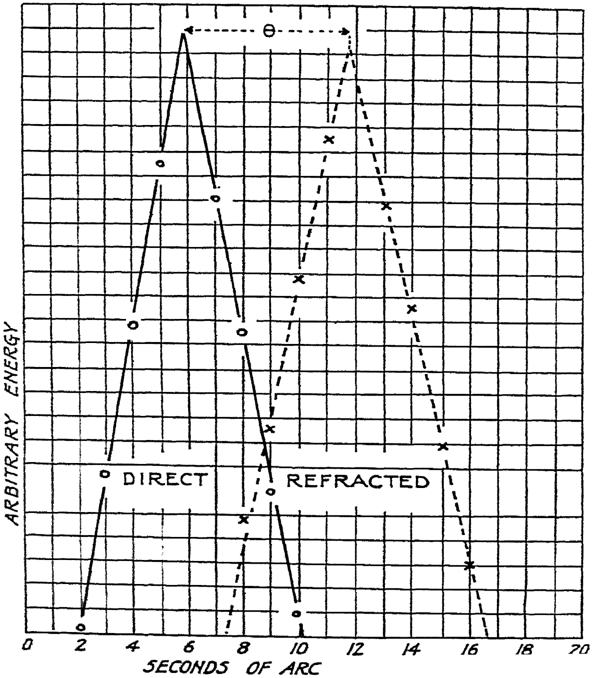


FIG. 32.—Refraction of X-rays by a prism (rocking curves).

The value of δ is most readily calculated from $n = 1 - \delta = \cos \rho$, where ρ is the internal glancing angle which the beam makes with the face AA′, and θ is the external angle. Assuming a single ray to be striking at A, and that the ray suffers no deviation at the first face, ρ and θ can be determined from ϕ, β and D, where D is the angle of deviation. Thus :

$$\phi = \theta + \beta, \text{ or } \theta = \phi - \beta,$$
$$\theta = D + \rho, \text{ or } \rho = \theta - D.$$

Substituting these values in the expression for n and solving for δ,

The values of D and ρ need a slight correction, 1/3″, on account of the deviation in passing through the first face. This is easily calculated.

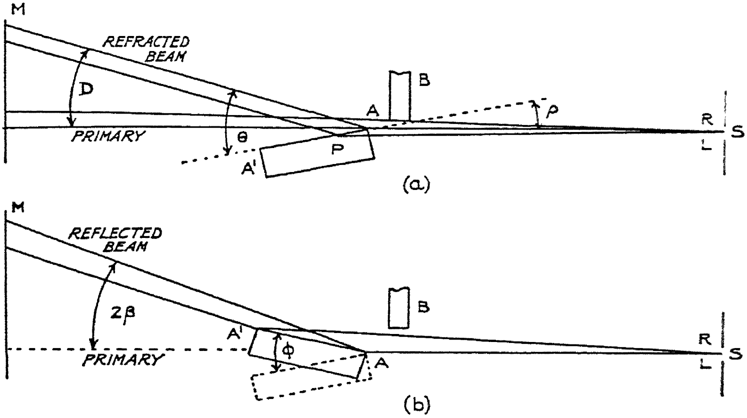


FIG. 33.—Total reflection of X-rays (Stauss).

All the various dispersion theories, that have been developed for the X-ray region, agree in the limiting case when the frequency of the radiation is greatly different from the natural frequencies of the medium. They all lead to the formula :

$$\delta = 1 - n = \overset{\mathrm{n}\mathbf{e}^2}{}$$

where **e** is the charge on an electron, m, its mass, ν, the radiation frequency, and n, the total number of electrons per cubic centimetre. Since δ is essentially a positive quantity, n is less than unity, and hence it should be possible to secure total reflection of X-rays at sufficiently small grazing angles, *i.e.*, within a limiting angle given by $\cos\theta_c = n$. Compton * calculated values of this critical angle, θ_c, for several substances and recently Kellermann † has also measured the refractive index of substances for X-rays, using a total reflection method. He employed a cylinder of the substance, the axis of which was at right angles to the beam of rays. With a wave-length of 1·537 Å. he obtained the following results :

Material.	Crown Glass.	Silver.	Glycerine.	$CaCl_2$ Solution.
θ_c	12·6′	25·5′	9·5′	10·4′
$\delta \times 10^6$	6·7	27·5	3·8	4·6

Attempts to measure the refraction of X-rays near the absorption limit are attended with great difficulties, but Larsson, Siegbahn and Waller ‡ have determined the disperson of X-rays in calcite and gypsum. Definite discontinuities were found both at the calcium λ, 3·063 Å., and at the sulphur, λ, 5·023 Å., critical absorption frequencies. The results show that the branches of the dispersion curves are rounded off, and do not approach infinity near the absorption bands.

Recently the dispersion curves for platinum, calcite and glass have been determined by Dershem, § who found that $\delta = 1 - n$ increases, approximately, with the square of the wave-length. This holds for regions not too close to critical absorption. It follows that δ/λ^2 should be constant. Derhsem found that this was the case for platinum and calcite. Similar results have also been obtained by Forster. ‖

Quantum theories of X-ray dispersion have been proposed by

---

* *Phil. Mag.*, **45**, 1121 (1923).

† *Ann. d. Phys.*, **4**, 185 (1930).

‡ *Phys. Rev.*, **25**, 235 (1925).

§ *Ibid.*, **33**, 659 (1929). See also Dershem and Schein, *ibid.*, **37**, 1246, (1931).

‖ *Helv. Phys. Acta.*, **1**, 18 (1928).

Wentzel,* Kramers † and others. Kronig ‡ has derived the expression :

$$\delta = 1 - n =$$

The summation is extended over r absorption bands, while the integration with respect to w is carried over each absorption band ; $a_r(w)$ is the atomic absorption coefficient whose value is $Cc^3Z^4 w^3$, where C is a constant, c, the velocity of light *in vacuo*, Z, the atomic number, ν, the incident frequency, w, the resonance frequency in the absorption band, and N, the number of atoms per unit volume. Kronig § quotes experimental results which favour his theory rather than the usual Lorentzian theory. On the other hand, Doane || determined the refractive index of silver for the K_{a1} line of M_o and concluded that his results support the Lorentz formula.

Since n is less than unity, the apparent velocity of X-rays in media is greater than that of radiation in free space. This is an interesting case of the difference between phase velocity and group velocity. The apparent increase of velocity is to be expected in the case where the frequency of the radiation is greater than that of the majority of the electrons in the matter which the rays traverse.

23. The Scattering of X-rays. Compton ¶ observed scattering phenomena with X-rays which could not be explained on the classical theory of scattering. He found that in addition to the scattered lines having the same wave-length as the primary rays, there were other lines displaced slightly towards the longer wave-lengths. This is known as the *Compton effect.*

X-rays proceeded from a molybdenum target T, Fig. 34, in the X-ray tube to the carbon scatterer, R, and were thence scattered at 90° with respect to the primary beam through slits 1 and 2 to

---

* *Zeits. f. Phys.*, **29**, 306 (1924).

† *Nature*, **114**, 310 (1924).

‡ *Journ. Opt. Soc., Amer.*, **12**, 551 (1926).

§ *Loc. cit.*

|| *Phil. Mag.*, **4**, 100 (1927).

¶ *Phys. Rev.*, **21**, 483 (1923).

the crystal of a Bragg's spectrometer, by means of which the wave-length of the X-rays that had been scattered through an angle of 90° was measured. In Fig. 35 are shown the complete spectra of both the primary and the scattered beam. The broken line represents the first and second order spectra of the direct rays, and the unbroken line the spectrum of scattered rays obtained under the same conditions. It is evident from the curves that the secondary X-rays do not possess a fixed wave-length, characteristic of the radiator, as do fluorescent rays, but that each line in the spectrum of the scattered radiation corresponds to a line in the primary beam.

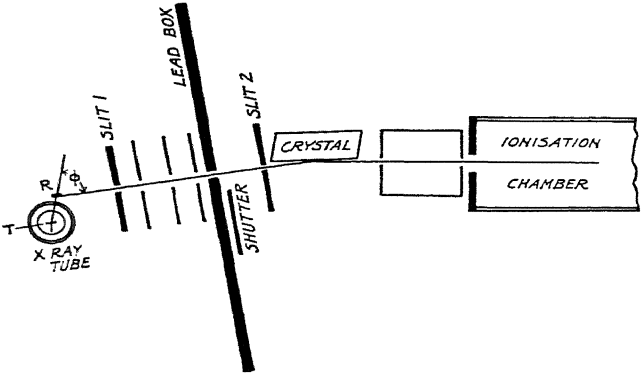


FIG. 34.—Scattering of X-rays. (Compton.)

Compton suggested that an electron, if it scatters at all, scatters a complete quantum of incident radiation. If we consider the primary rays to proceed in quanta, so definitely directed that they can be scattered by individual electrons along with their energy $h\nu$, they will carry momentum $h\nu/c$. The scattered quantum, however, proceeding in a different direction from the primary, carries with it a different momentum. Thus, by the principle of conservation of momentum, the electron which scatters the ray must recoil with a momentum equal to the vector difference between that of the primary and that of the scattered quanta. But this energy of the recoiling electron is taken from that of the primary quantum, leaving a scattered quantum which has less energy, and hence a lower frequency than has the primary.

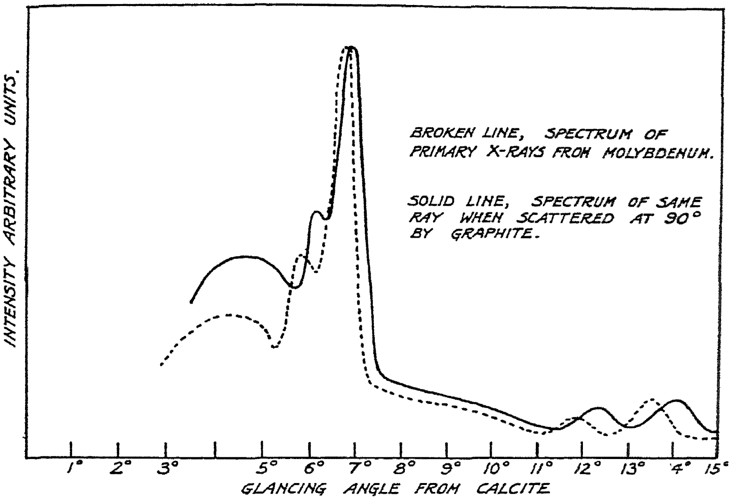


FIG. 35.—Spectra of primary and scattered X-rays.

From the conservation of momentum and energy principles Compton deduced the formula :

$$\frac{1}{\nu'} - \frac{1}{\nu} = \frac{2h}{m_0c^2}\sin^2\frac{\theta}{2},$$

or, in terms of wave-lengths :

$$\lambda' = \lambda + \frac{2h}{m_0c}\sin^2\frac{\theta}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where λ' is the wave-length of the scattered radiation, λ, that of the primary, m_0, the mass of the electron moving with a velocity very small compared with that of light, c, and θ is the angle of scattering.

Thus $\lambda' > \lambda$, the increase ranging from a few per cent. for X-rays of medium wave-length to more than 200 per cent. in the case of γ rays scattered backwards ($\theta = \pi$). The increase of wave-length of the scattered radiation is independent of the wave-length of the primary. Compton found that in the case of the K-rays from molybdenum, scattered by graphite, the wave-length of the unmodified K_α line was 0·708 Å., while the wave-length of the scattered ray was equal to 0·730 Å., *i.e.*, $\lambda' - \lambda = 0{\cdot}022$ Å. According to the theory it should be 0·024 Å. Experiments by many workers * have confirmed both Compton's theory and equation (15).

The velocity of recoil of the electron is βc where

$$\beta = \frac{2\alpha \sin\frac{\theta}{2}\sqrt{1 + (2\alpha + \alpha^2)\sin^2\theta/2}}{1 + 2(\alpha + \alpha^2)\sin^2\theta/2} \quad . \quad . \quad (16)$$

α being equal to h:

Wilson † and Bothe ‡ independently discovered, with the aid of Wilson's cloud apparatus, the recoil electrons, their presence being indicated by very short tracks within the primary beam. With hard X-rays these short tracks increase in length, and develop tails on the side of the incident X-rays, and for this reason Wilson has called them *fish tracks*. Wilson and Bothe both conclude that the direction and range of these fish tracks are in agreement with the view that they are due to electrons which have recoiled from quanta, scattered by the electrons.

From equations (15) and (16) Compton calculated that for incident radiation of intensity I_0, the intensity, $I(r, \theta)$, of the radiation scattered in a direction θ by N electrons is, at a distance r, given by :

$$I(r,\theta) = I_0 \frac{Ne^4}{2r^2m^2c^4} \cdot \frac{1 + \cos^2\theta + 2\alpha(1 + \alpha)(1 - \cos\theta)^2}{[1 + \alpha(1 - \cos\theta)]^5}$$

---

* See Kallmann and Mark, *Naturwiss.*, **13**, 297 (1925); Sharp, . *Rev.*, **26**, 691 (1925); Gingrich, *ibid.*, **36**, 1050 (1930).

† *Proc. Roy. Soc.*, *A*, **104**, 1 (1923).

‡ *Zeits. f. Phys.*, **16**, 319 (1923).

Other formulæ have been proposed by Debye,[*] Jauncey,[†] Woo,[‡] Breit,[§] Dirac [||] and Klein and Nishina.[¶] Dirac calculated the magnitude of the Compton effect with the aid of the new quantum mechanics. He finds that for plane-polarised incident radiation of intensity I_0, the scattered radiation at a distance, r, in a direction whose polar angles are θ, ϕ, is :

where θ is the angle of scattering and ϕ, the angle between the direction of the scattered radiation and the direction of the electric vector of the incident radiation.

For unpolarised incident radiation Dirac deduces :

$$\{1 + \alpha(1 - \cos\theta)\}^3 \quad . \quad .$$

The full curve of Fig. 36 shows the variation with θ of the intensity of the scattered radiation according to Dirac's formula (18) for unpolarised incident radiation of wave-length 0·022 A., *i.e.*, $\alpha = 1{\cdot}2$. The lower broken curve gives the results of Compton's light quantum theory and represents his formula (17), the crosses indicating his experimental values. The upper dotted curve is deduced from the classical theory which expresses $I(r, \theta)$ as :

$$I_0 \frac{Ne^4}{\text{[illegible]}} (1 + \cos^2\theta)$$

The photon, or corpuscular, theory predicts quantitatively, and in detail, the change of wave-length of the scattered X-rays and the characteristics of the recoil electrons, but the classical theory is altogether helpless to deal with these phenomena. The unmodified line is probably due to X-rays, which are scattered by electrons, so firmly held within the atom, that they are not ejected by the impulse from the deflected photons.

From the Compton effect, therefore, we conclude that radiation consists of directed quanta of energy, *i.e.*, photons, and that energy and momentum are conserved when these photons interact with electrons and atoms. This does not mean that there is no truth in the concept of waves of radiation, but whether the waves serve to guide the photons, or whether there is some other relation between photons and waves, is another and difficult question.

---

[*] *Phys. Zeits.*, **24**, 161 (1923).
[†] *Phys. Rev.*, **25**, 723 (1925) ; **37**, 1193 (1931).
[‡] *Ibid.*, **25**, 444 (1925).
[§] *Ibid.*, **27**, 362 (1926).
[||] *Proc. Roy. Soc.*, *A*, **111**, 405 (1926).
[¶] *Nature*, **122**, 399 (1928).

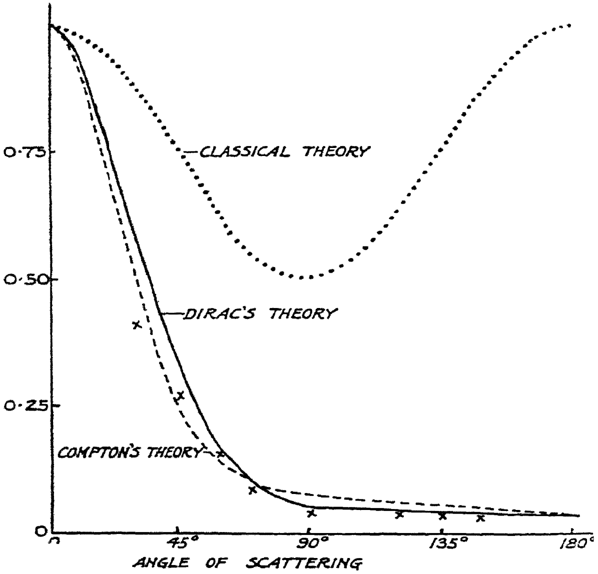


FIG. 36.—The intensity of scattered X-ray radiation.

24. X-ray Diffraction in Liquids. Debye and Scherrer * found that when X-rays were passed through certain liquids, a diffraction halo was produced. Other workers † discovered that in some cases a second halo was present besides the chief halo, or ring, characteristic of the molecules of the scattering substance. For example, Tonaka and Tsuji * noted that dilute aqueous solutions give a pattern consisting of an outer ring due to water, and a corona round the central spot. With increasing concentration, the intensity of the corona gradually increases, and finally develops into a halo. Good † observed two maxima with water. This result he explains by supposing that there are temporary associations of water molecules to form rudimentary ice crystals, which therefore have a grating constant. The water thus consists at any moment of ice-crystals, together with randomly-orientated water molecules.

---

* *Nachr. Gesell. Wiss. Göttingen*, 6 (1916).

† See Keesom and Smedt, *Proc. Roy. Soc. Amsterdam*, 25, 118 (1922); **26**, 12 (1923)

Stewart and his co-workers ‡ have reported the diffraction effects in many organic liquids.

Raman and Ramanathan,§ Debye,‖ Zernicke and Prins ¶ have suggested theories to explain the phenomena. In general we may say that the form of the X-ray liquid diffraction pattern is interpreted as being primarily due to the arrangement of the molecules in the liquid, the arrangement of the atoms in the molecule and the electrons in the atom producing secondary effects.

Stewart and his school ** suggest that every liquid contains a myriad of small groupings of molecules, produced by forces acting between them, the groups being neither perfect in form nor permanent. The word *cybotapis*, which means literally "space arrangement," has been adopted to designate this condition in a liquid. A crystal is approximately perfect only in fragments, but a liquid goes to a much greater extreme, for its semi-perfect small groups do not even retain their identity. The theory of diffraction in such a physical structure cannot be exactly that of crystal powders, or of unorganised molecules. But the crystal powder theory may be accepted as applicable to an idealised condition to which the liquid state only approximates at any instant. In such a theory Bragg's law holds for the intense first order diffraction band, provided the beam is monochromatic. The conception of molecular non-crystalline groupings in a liquid explains all the phenomena associated with the diffraction of X-rays in liquids.

---

* *Kyoto Coll. Sci. Mem.*, **13, 27 (1930).**

† *Helv. Phys. Acta.*, **3, 205 (1930).**

‡ *Phys. Rev.*, **30, 232 (1927) ; 31, 1, 10, 174 (1928) ; 32, 153 (1928).**

§ *Proc. Ind. Assoc. Culv. Sci.*, **8, 127 (1923).**

‖ *Journ. Math. Phys.*, **4, 133, (1925).**

¶ *Zeits. f. Phys.* **41, 184, (1927).**

** *Loc. cit.*

25. Gamma-rays. Gamma (γ) rays are intermediate in wave-length between X-rays and cosmic rays. They were first investigated by Rutherford and Andrade[*] by means of the crystal method, which is somewhat similar to that used in the investigation of the wave-length of X-rays.

Thibaud[†] studied the various frequencies of a complex γ-radiation converting this radiation by means of photoelectric effects into β-ray spectra, and measuring the energies of the various electronic streams emitted. He also employed the rotating crystal method and photographic registration, but as the wave-length of the γ rays is very small, the grazing angle for selective reflection is not greater than a fraction of a degree. A fine beam of γ-rays impinged on a crystal of rock-salt, carried on a gonometer and rotating with angular velocity of less than 1° in twenty-four hours. The dispersion was fairly large, as the distance from the crystal to plate was 45 to 65 cm., and the exposure required was 40 to 200 hours. The sources of γ-radiation employed were 40 mg. of radium bromide in equilibrium, a preparation of mesothorium with a total activity equivalent to that of 15 mg. of radium bromide, and also 49 millicuries of radiothorium. The γ-rays gave fine line-spectra without any appearance of continuous bands, and the following wave-lengths were observed using the tube of radiothorium:

Nos.	λ in Å.	Energy (volts).[‡]	Origin.
1	0·168	73,500	Rd Th
2	0·145	85,000	,,
3	0·062	198,600	Th B
4	0·052	236,000	,,

---

[*] *Phil. Mag.*, 28, 262 (1914).

[†] *Comptes Rendus*, 180, 138 (1925); *Ann. de Physique*, 5, 73 (1926).

[‡] Calculated from the formula $Ve = h\nu$, where V is the potential difference through which the electronic charge e falls. If V is expressed in volts this gives,

$$\lambda = \frac{3 \times 10^{10} \times 6{\cdot}55 \times 10^{-27}}{V \times 1{\cdot}59 \times 10^{-12}} = .$$

Frilley * has recently made great progress in detecting γ-radiations of high frequency with the aid of the revolving crystal method, the crystal being of rock-salt. Radon was used as a source, and lines due to γ-rays from Ra B and Ra C, lying between 35 and 284 X.U., were photographed (1 X.U. $= 10^{-11}$ cm.). In later work he was able to measure a γ-ray of $7{\cdot}7 \times 10^5$ volts energy, *i.e.*, a wave-length of about 16 X.U. This radiation has a glancing angle of less than 10 minutes and is relatively feebly scattered by the crystal.

The apparatus consisted of three carriages mounted on a rigid steel bench, 1·50 metres long, holding the source, crystal and plate, respectively. In front of the source was arranged a lead slit, and the carrier for the rock-salt crystal was capable of adjustments in all directions. Two photographic plates were used, placed face to face with an intensifying screen of calcium tungstate between them, and they were protected from stray radiations by screens of lead. The crystal was rotated slowly during the exposure, following the usual technique, and while the strongest lines could be obtained with 100 mg. and a rotation of 2° in twenty-four to forty-eight hours, the weaker lines required 200 to 300 mg. with a rotation of only 30′ in twenty-four hours.

Comparison of the results obtained by Thibaud and by Frilley lead to a most important and convincing proof of the validity of the Einstein photo-electric equation for these high frequencies.

The character of the γ-ray emission from a radio-active body has also been investigated by the absorption method. The source is placed close to an electroscope and the change in the ionisation current, when different thicknesses of lead or aluminium are interposed, is observed. It is generally found that after the absorbing medium has reached a certain thickness, the curve becomes approximately exponential. This part of the curve is extrapolated back to zero thickness, according to the same law, and is subtracted from the original readings. The new absorption curve for the softer fraction of the radiation is then treated in the same way. In this manner it is possible to analyse the experimental curve into a series of exponentials whose individual coefficients then serve to describe the original complex radiation.

---

* *Comptes Rendus,* **186, 137, 425 1614 (1928)** ; *Ann. de Physique,* **11, 483 (1929).**

Gray[*] showed that when homogeneous γ-rays are scattered, there is a change of quality, *i.e.*, wave-length, and the change of wave-length is more pronounced, the greater the angle of scattering. This is an example of the Compton effect[†].

Scattering of γ-rays with change in wave-length is also shown by Skobelzyn's experiments.[‡] He passed the γ-rays of radium C through an expansion chamber and obtained tracks of high-speed electrons, which are associated with the scattering. Hoffmann[§] attempted to determine the change of wave-length directly by observing the absorbability of the γ-rays from radium (B + C), filtered through 1 cm. of lead, after scattering from carbon at various angles.

Many attempts have been made to deduce a theoretical formula for the intensity of scattering. Of these formulæ the most frequently used are those of Compton, Dirac and of Klein and Nishina.[‖] They agree in postulating that all the electrons in an atom scatter equally and independently, so that it is sufficient to give a scattering coefficient per electron. The Klein-Nishina formula is to be preferred on theoretical grounds.[¶]

26. Cosmic Rays. In recent years there has been a rapid growth in our knowledge of new types of electromagnetic radiations of very short wave-lengths, which are able to penetrate great thicknesses of matter, before they are absorbed. This type of ultra-penetrating radiation, known as *cosmic rays*, has about 100 times the penetrating power of γ-rays, and the frequency of these cosmic rays is from 100 to 1,000 million times greater than that of visible light.

For many years it has been known that there is always a small amount of residual ionisation in an electroscope, due to some highly penetrating rays, which can pass through metal walls, 1 cm. thick, and ionise the gas inside.

---

[*] *Phil. Mag.*, 26, 611 (1913).

[†] See Section 23.

[‡] *Zeits. f. Phys.*, 43, 354 (1927); 58, 595 (1929).

[§] *Ibid.*, 36, 251 (1926).

[‖] See Section 23.

[¶] For the various methods used in measuring the scattering see "Radiations from Radioactive Substances," Rutherford, Chadwick and Ellis.

In making a measurement of the penetrating radiation an electroscope is charged to a known potential, and the drop in potential of the insulated fibre during a given time interval is noted. From these data, and the known capacity of the fibres, together with the volume of the enclosed air in the electroscope and the charge on an electron, the rate of production of ions per unit volume can be calculated. The ionisation is measured at the surface of a snow-fed lake, situated at a considerable altitude, and by sinking the electroscope in the lake, the absorption of the radiations in water is determined. A snow-fed lake is chosen because the water is free from contamination by radioactive substances. In practice, the electroscope, filled with gas at a high pressure, is left in the water for about twelve hours. It is then brought quickly to the surface, and read. A small correction is applied for the discharge during lowering and

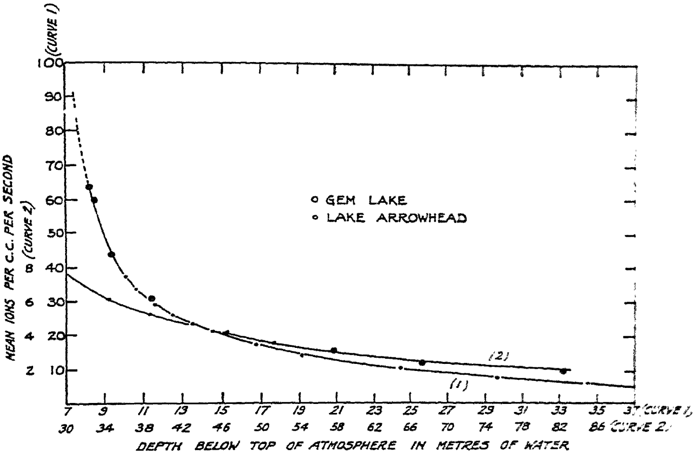


FIG. 37.—Depth-ionisation curve for cosmic rays.

raising, but these corrections are small and quite accurately obtainable.

Millikan and his co-workers,* the pioneers in this type of research, first measured the absorption of the rays in Lake Muir, and proved that the origin of the rays is outside the atmosphere.

More recently, Millikan and Cameron † have published the results of further observations with a more sensitive type of electroscope. Their results are shown in Fig. 37; Gem Lake being at an altitude of 9,120 feet, the readings extend from a level equivalent to 8·25 metres of water beneath the top of the atmosphere down to a level of 80 metres beneath the upper limit of the atmosphere. The observed rate of discharge of the electroscope changed by more than thirty-fold, namely, from a value represented by an intensity of ionisation within the electroscope of 64·1 ions per c.c. per second down to 2 ions per c.c. per second.

The absorption coefficients, as computed at successive points along this curve, are shown in the following table:

Depth in Metres of Water beneath Top of Atmosphere.	Absorption Coefficient, σ.	Depth in Metres of Water beneath top of Atmosphere.	Absorption Co-efficient, σ.
8·25– 9·5	0·27	20–30	0·045
9·5 –10·5	0·16	30–40	0·038
10·5 –11·5	0·11	40–50	0·028
11·5 –12·5	0·095	50–60	0·028
12·5–15·0	0·067	60–80	0·028
15·0–20·0	0·058		

At great depths, *i.e.*, between 40 and 80 metres, the readings are so consistent as to show that even a blanket of 80 metres of water is insufficient completely to absorb the cosmic rays. The curve has here reached a value of 2 ions per cubic centimetre per second, but is still falling. In order to find the zero of the instrument, or the ionisation when all external rays have become absorbed, and at the same time the absorption coefficient of these

'hys. Rev., 27, 353, 645 (1926).

† *Ibid.*, 37, 235 (1931).

hardest rays, the curve was analysed by trial and error method, and it was found that a single coefficient of absorption was adequate to explain the curve over the whole range between 40 and 80 metres, the value of the absorption coefficient being 0·028. The existence of such a coefficient means that a hundred metres farther down, *i.e.*, at 180 metres, an ionisation of about 0·03 ions per cubic centimetre per second should be observable by an instrument capable of detecting such an amount.

Regener* has reported water observations made in Lake Constance. His ionisation chamber was a steel bomb holding 39 litres of CO_2 gas at a pressure of 30 atmospheres. A central electrode was connected to an electrometer, which was initially charged to 600 volts. Every hour the fibre of the instrument was photographed in the position to which it had drifted owing to the loss of voltage, due to ionisation. By zinc plating the inside of the bomb, and by carefully purifying and drying the contained gas, there was scarcely any trace left of ionisation due to the material of the apparatus itself. With the apparatus 32·4 metres below the surface the recorded positions of the fibre were about five times as far apart as at a depth of 230·8 metres. This means that the loss of voltage in the first case was about five times as great in an hour as in the second case. The losses are given as 4·33 and 0·83 volts, respectively. In the following table the loss in volts per hour is shown, after deduction of the loss caused by the apparatus itself. At the surface of the water the hourly loss was about 40 volts.

Depth in metres.	32·4	78·6	105·2	153·5	173·6	186·3	230·8
Volts per hour .	3·55	0·87	0·53	0·22	0·15	0·106	0·051

It is to be noted that the decrease of ionisation continues to a depth of 230 metres. Utilising the absorption coefficient, deduced from the above results, the wave-length of the hardest, *i.e.*, the shortest wave-length, component of the penetrating radiation was calculated to be from $4{\cdot}6 \times 10^{-13}$ to $0{\cdot}6 \times 10^{-13}$ cm., according to the formula used.

---

* *Naturwiss.*, **15**, **183** (**1929**).

While Lake Constance receives much water from glaciers, brought to it by the Rhine, it is by no means free from the suspicion of having in its basin radioactive matter. Accordingly, Regener* repeated his observations, taking special precautions to protect the ionisation chamber from possible variations of radioactivity with depth. The existence of a penetrating component of cosmic radiation, for which $\sigma = 0{\cdot}018$ per metre of water, was verified. Observations were made at various depths down to 237 metres. Analysis of the absorption curve shows four components, the relative intensities on entering the atmosphere and the absorption coefficients (per metre of water) of which are, respectively, 0·81 and 0·020, 6·4 and 0·073, and 16·35 and 0·21. The wave-length of the hardest rays, deduced from Klein and Nishina's formula,† is $0{\cdot}63 \times 10^{-13}$ cm., whilst the coalescence of a proton with an electron and the conversion of their energy into radiation would give rise to radiation corresponding to a wave-length of $1{\cdot}313 \times 10^{-\ 5}$ cm.

From an analysis of the curve shown in Fig. 37, Millikan and Cameron have concluded that, to account for the peculiar bend in the curve between 10 and 12 metres, it is necessary to suppose that the cosmic rays consist of three bands of different wave-lengths having, approximately, the relative frequencies 1, 4, 8, and the shape at great depths requires the introduction of a fourth band. The coefficients of absorption of these four sets of waves are 0·80, 0·20, 0·10 and 0·028, respectively. The sudden change in the value of σ, at about 11 metres, means that at this point a band of long wave-length, or of relatively large absorption coefficient, is disappearing, and one of much shorter wave-length remains to cause the bulk of the ionisation. The wave-lengths corresponding to these values of the absorption coefficients are $1{\cdot}7 \times 10^{-3}$ Å., $4{\cdot}23 \times 10^{-4}$ Å., $2{\cdot}11 \times 10^{-4}$ Å. and $5{\cdot}92 \times 10^{-5}$ Å., respectively.

Within the limits of observational uncertainty these rays show a uniformity of distribution, *i.e.*, an independence of both latitude and of sidereal time. Both of these conclusions had been established by Millikan and Cameron,[*] but other workers obtained different results. Recent work by Steinke[†] and Hess,[‡] however, has confirmed the independence.

---

* *Phys. Zeits.*, **31**, 1018 (1930) ; *Nature*, **127**, 233 (1931).

† *Nature*, **122**, 399 (1928).

Although, taking Millikan's view, we have supposed that the cosmic rays are electromagnetic radiations, the fundamental possibility of electronic radiation has been pointed out by nearly all the workers concerned. For example, Skobelzyn,[§] using Wilson's cloud apparatus, has demonstrated the presence of electrons moving with high speed and not of radioactive origin. Wilson[¶] has also pointed out that β particles of sufficient energy could produce most of the phenomena observed in connection with the penetrating radiation, and there may well exist conditions in thunderstorms, where β particles may acquire the necessary great energies of more than 10^9 volts. Bothe and Kolhörster[**] found that the radiation is not equally distributed in all directions, but is strongest in the vertical direction. They suggest that the rays are corpuscular in nature. Epstein[††] has shown that in order to satisfy Millikan's observation of the uniform intensity of the cosmic rays over the earth, they might be (*a*) electromagnetic rays of cosmic origin, (*b*) corpuscular rays of higher energy than 10^9 volts, at least 6×10^9 volts, of cosmic origin, (*c*) corpuscular rays of terrestrial origin. The third source of origin is doubtful as Hulburt[‡‡] has shown that in this case the penetrating radiation would be most intense at low latitudes and feeble at high latitudes.

Rossi's results[§§] have confirmed the existence of the penetrating corpuscular rays observed by Bothe and Kolhörster, but Brüche[||||] has concluded that only rays whose mean velocity is very little less than the velocity of light can reach the mean latitudes of the earth.

---

[*] *Phys. Rev.*, **31**, 163 (1928).
[†] *Zeits. f. Phys.*, **42**, 570 (1927).
[‡] *Wien. Ber.*, **137**, 327 (1928).
[§] *Proc. Roy. Soc.*, *A*, **109**, 206 (1925).
[||] *Zeits. f. Phys.*, **54**, 686 (1929).
[¶] *Camb. Phil. Soc. Proc.*, **22**, 534 (1926).
[**] *Zeits. f. Phys.*, **56**, 751 (1929).
[††] *Proc. Nat. Acad. Sci.*, **16**, 658 (1930).
[‡‡] *Phys. Rev.*, **37**, 1 (1931).
[§§] *Zeits. f. Phys.*, **68**, 64 (1931).
[||||] *Phys. Zeits.*, **32**, 31 (1931).

Millikan and Cameron present striking quantitative evidence that the strongest, and most absorbable cosmic ray frequencies arise from the act of formation of helium out of hydrogen. The three more penetrating bands are due to the formation from hydrogen of the only other abundant elements, oxygen (C, N, O), silicon (Mg, Al, Si, S) and iron (iron group). Millikan supposes that the constancy in distribution of the cosmic rays must mean that the temperature existing even in the atmosphere of the sun, whence alone they could get to us from this star, is inimical to the union of hydrogen into the heavier elements, for hydrogen is present in enormous quantity in the sun's atmosphere. In addition, the cosmic rays cannot originate in any places in the universe from which they are obliged to come to us through any appreciable amount of matter. If they had done so, they would, on entering the earth, be partly β-rays and partly photons, and on account of the earth's magnetic field, the β-ray part would of necessity be stronger near the magnetic poles than at lower latitudes. But no trace of such an influence can be discovered.

Jeans* has criticised Millikan's suggestion that the hardest radiation of all has its origin in the synthesis of iron. He points out that if the annihilation of matter is the true origin of the two hardest constituents of the cosmic radiation, it would seem likely that these, and these alone, form the fundamental radiation, and that all other constituents represent mere softened, or degraded forms of these two components.

On the whole, therefore, neither the nature, nor the origin of cosmic rays is definitely settled.

27. The Velocity of Light. During recent years Michelson † has measured the velocity of light at Mount Wilson under more favourable conditions, as regards accuracy, than have hitherto been obtained. A beam of light was reflected from a rotating octagonal mirror to a mirror in Mount San Antonio twenty-two miles away, and after reflection from the latter impinged on the next succeeding face of the rotating mirror, from whence it was reflected into a micrometer eyepiece. This was accordingly almost a null method as regards deflection, and attention was concentrated on measuring the speed of rotation of the mirror. which was synchronised with a fork, controlled by comparison with a pendulum. Later,* he used in turn five different revolving mirrors of glass, or steel, each with from eight to sixteen facets. The results for the velocity of light *in vacuo*, given by the separate mirrors, show a remarkable agreement as follows:

---

* *Nature*, 127, 594 (1931). For further details of cosmic rays the reader may consult the report of a discussion on the subject, *Proc. Roy. Soc. A.*, 132, 331 (1931).

† *Ast*

Glass	8	facets	299,797 km. per sec.
Steel	8	,,	299,795 ..
Glass	12	,,	299,796 ..
Steel	12	,,	299,796 ..
Glass	16	,,	299,796 .,

The mean result is 299,796 ± 4 km. per sec.

Michelson and Gale † determined the effect of the earth's rotation on the velocity of light: Two beams of light were caused to travel in opposite directions through a rectangle of 12 inch water pipe, of total path length somewhat over a mile, and brought to interference. Sharp steady fringes were produced when the air pressure was reduced below an inch of mercury. The beam going counter-clockwise around the rectangle was retarded, giving an observed fringe displacement of 0·230 ± 0·005. This agrees with the value (0·236 ± 0·002) computed on the hypothesis of a fixed ether, and is also in accord with relativity, so the experiment in this sense is not a critical one. What it does prove is that, if there is an old-fashioned ether, it does not rotate with the earth.

Relativity will not fare so well if the results reported by Miller ‡ for his repetition of the Michelson-Morley experiment are eventually established beyond question. He made thousands of ether drift measurements both at Mount Wilson and at Cleveland, using every precaution to eliminate mechanical disturbances, as well as other possible sources of error. He concludes that a positive result is shown by all the Cleveland observations and a somewhat larger effect at Mount Wilson, amounting at the latter place to about 9 km. per sec., or one-third the orbital motion of the earth, indicating a partial drift of the ether with respect to the earth which increases with the altitude. After completing his computations Miller[*] considered that the variation of the effect with altitude was within the limits of experimental error, and therefore doubtful. The observations are consistent with a definite absolute motion of the earth through space, combined with the periodic changes due to its orbital motion.

---

* *Astrophys. Journ.*, **65**, 1 (1927).
† *Ibid.*, **61**, 140 (1925).
‡ *Proc. Nat. Acad. Sci.*, **11**, 306 (1925).

Miller's original assumption of a direct determination of ether drift has been criticised by Eddington[†] and by Swann,[‡] and the most probable explanation of the experimental results is obscure. Kennedy[§] has repeated Miller's work with an improved form of apparatus and has obtained no evidence of ether drift.

Similar conclusions of no ether drift have been reached by Tomaschek[‖] and Chase.[¶] The apparatus used by the latter could have detected an ether-drift velocity of 3 km. per sec. Piccard and Stahel[**] carried out experiments on the summit of the Rigi in Switzerland (altitude 1,800 m.). They used a self-recording interferometer with thermostatic temperature control. The results were completely negative, the ether drift being only one-fortieth part of that expected by Miller.

Gleich,[††] however, maintains that the correct result of the Michelson experiment is still an open question, though the Lorentz transformation and the whole theory of relativity are based on the supposed negative result, that is to say, no "ether drift" or possibly no ether. If the ether is to be regarded as fixed in space, there will be a daily varying ether drift to be considered in the Michelson experiment, a yearly varying drift and a constant drift depending on the motion of the solar system through space ; it is only the latter which can have a perceptible effect, as the others are too small.

---

[*] *Astrophys. Journ.*, **68**, 341 (1928). This reports a conference on the Michelson-Morley experiment.

[†] *Nature*, **115**, 870 (1925).

[‡] *Ibid.*, **116**, 785 (1925).

[§] *Proc. Nat. Acad. Sci.*, **12**, 621 (1926)

[‖] *Ann. d. Phys.*, **78**, 743 (1926).

[¶] *Phys. Rev.*, **30**, 516 (1927).

[**] *Naturwiss.*, **16**, 25 (1928).

[††] *Zeits. f. Phys.*, **59**, 132 (1929).

Very recently Joos * has shown that the velocity of the earth with respect to the ether, if it exists, cannot be greater than 1·5 km. per sec.

BIBLIOGRAPHY

BRAGG, W. H. "Introduction to Crystal Structure."
BRAGG, W. H. and W. L. "X-rays and Crystal Structure."
BUCKINGHAM. "Matter and Radiation."
COMPTON. "X-rays and Electrons."
DE BROGLIE. "X-rays."
LECOMTE. "Le Spectra Infra-rouge."
LYMAN. "The Spectroscopy of the Extreme Ultra-violet."
RAWLINS and TAYLOR. "Infra-red Analysis of Molecular Structure."
RUTHERFORD, CHADWICK and ELLIS. "Radiations from Radioactive Substances."
SCHÆFER and MATOSSI. "Das Ultrarote Spektrum," "Der Ramaneffect."
SIEGBAHN. "The Spectroscopy of X-rays."
"Transactions of the Faraday Society," **25**, 611 (1929).

---

* *Ann. d. Phys.*, **7**, 385 (1930).

CHAPTER VII

MAGNETISM

1. The Magnetic Properties of Atoms. According to the older quantum theory, an atom consists of a heavy nucleus, with a positive charge, and a number of electrons moving in orbits about the nucleus as centre of force. These electrons can circulate in closed orbits without radiating energy at all, whereas classical theory indicates that every acceleration of an electron must be accompanied by radiation. In addition, of all the infinite number of different orbits which, according to the classical theory are possible, only certain discrete orbits are permitted, these permitted orbits being determined by certain quantum conditions. An atom, in which electrons are describing orbits permitted by the quantum conditions, is said to be in a stationary state; and to each particular stationary state pertains a certain energy. Under certain conditions an atom can pass from a stationary state, energy E_1, to another stationary state of less energy, E_2, and this sudden passage is accompanied by a radiation of energy $E_1 - E_2$, of which the frequency, ν, is given by the condition:

$$h\nu = E_1 - E_2,$$

where h is Planck's constant.

These stationary states are defined by a fundamental postulate which may be expressed in the form:

$$\oint \mathrm{p}d\mathrm{q} = \mathrm{n}h,$$

where the integral is to be taken over a complete period, p and q are the conjugate momentum and co-ordinate, respectively, and n is an integer.

Fresh light has been thrown on the problems of atomic magnetism by the new quantum mechanics, although the latter gives a less definite picture of the atom than that of Bohr. The hydrogen atom is regarded as a nucleus, surrounded by a space charge, determined by quantum numbers which emerge in a natural way from the derived equations. An alternative treatment reg the hydrogen atom as a centre of force surrounded by a field of probability, *viz.*, the probability of the electric charge which constitutes the negative electron being found within any assigned region. The quantum numbers then define the characteristics of the probability field, and although there is close similarity between some of the formal treatment of the older and newer theories, the interpretations are different.

Associated with each electron in an atom is a set of quantum numbers; n, the total quantum number, l, a subsidiary quantum number which is less by unity than the azimuthal quantum number, k, of the older theory, *i.e.*, $l = k - 1$. In addition, to each electron is assigned a quantum number, s, defining the spin of the electron. For a single electron, $s = \pm \frac{1}{2}$ so that the angular momentum of spin is $\frac{1}{2}(h/2\pi)$, where $h/2\pi$ is the *quantum unit of angular momentum.* This so-called spin forms an important postulate in the new quantum mechanics. Eddington * has shown that the angular momentum of the electron is composed of two parts, one being the angular momentum postulated in the older quantum theory, and the other, the spin of the electron which must be added to the orbital momentum. The idea of the spinning electron has explained certain discrepancies between theory and experiment, the so-called *duplexity* phenomena, where the observed number of stationary states for an electron in an atom are twice the number given by theory.

In the atom the effects of the constituent electrons are additive, so that the total angular momentum—and magnetic moment—of an atom is a resultant of the orbital and spin moments of the electrons. In general, the orbital moments may be regarded as combining to give a resultant, characterised by the quantum number l, and the spins to a resultant s. The total angular momentum of an atom is indicated by the quantum number j, and j is the resultant of l and s, assuming values from $l + s$ to $l - s$ at intervals of 1.

Now the possible states of an atom are characterised by terms which are classified as S, P, D, F, *etc.*, according as $l = 0, 1, 2, 3,$

---

* *Proc. Roy. Soc., A,* **126**, 696 (1930).

etc., and each term may be multiple, the multiplicity r being such that $r = 2s + 1$. The spectroscopic symbol ${}^{r}L_{j}$, *e.g.*, ${}^{4}F_{9/2}$, thus gives the spin moment s ($r = 2s + 1$), the orbital moment l (*e.g.*, for F terms $l = 3$), and the total moment j.

From an analysis of the line spectrum, emission or absorption, of an element, it is possible to deduce the ground term, corresponding to the deepest state, or normal state, of the atom of the element. In many cases, however, the normal spectroscopic state is not known from direct experiment, but it may be predicted with reasonable certainty by the aid of rules, which were primarily suggested by experimental facts, but which also have theoretical justification. The importance of determining the ground term lies in the fact that the magnetic moment of an atom (or ion) may be calculated when its normal spectroscopic state is known.

The Zeeman effect has thrown much light on atomic magnetism. A magnetic field splits each spectral line into three, when the line is viewed at right angles to the field ; the central one is polarised parallel to the field, and the two outer ones at right angles to the field. The central one is of the same wave-length as the original line, and the outer ones equidistant from it. Now the effect of a field H is to cause what is known as the *Larmor precession* of the orbit of the electron about the axis of the field, and the frequency of this precession is o, where

$$eH$$

$$o =$$

e being the charge on an electron, m_0, its mass and c, the velocity of light.

If E_0 is the energy of the electron in the absence of the magnetic field and E' the increase of energy due to o, then E, the energy in the presence of the field, is given by :

$$E = E_0 + E' = E_0 + moh,$$

m being a *magnetic quantum number*. Thus the frequency, ν, due to a transition where m changes to m′ is,

$$\nu = \frac{1}{h}[(E_0 + moh) - (E_0' + m'oh)],$$

or,
$$\nu = \nu_0 + o(m - m'),$$

where ν_0 is the frequency of the original line. Now m changes by $\pm$ 1 or 0, so that the *normal Zeeman triplet* is given by:

$$\nu - \nu_0 = \pm o, \text{ or zero,}$$

and the magnitude of separation of the outer lines from the central one is $\delta\nu = o$.

The orbital motion of the electrons in an atom produces a magnetic field of such a kind that the atom may be considered as a permanent bar magnet, when discussing its behaviour in an external field, constant in time and uniform in space.

Let us consider first an atom with only one electron, and neglect the intrinsic magnetic moment of the electron due to its spin. According to Kepler's law of area, the rate, dA/dt, at which the radius, r, drawn from the nucleus to the electron, describes area is such that,

$$2m_0\frac{dA}{dt} = m_0 r^2 \frac{d\phi}{dt} = \mathrm{p},$$

where ϕ is the azimuthal angle and p, the angular momentum. Integrating for one complete period T, we obtain:

$$\text{area of orbit} = A = \frac{\mathrm{p}T}{2m_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to quantum conditions, the angular momentum, p, of any atom is:

$$\frac{\mathrm{j}h}{2\pi},$$

where j is an integer, or an integer plus $\frac{1}{2}$, and is called the *inner quantum number*. The total angular momentum of an atom is to be found by taking the vector sum of the spin and orbital moments, and equation (1) may be written in the form:

$$A = \frac{\mathrm{j}hT}{4\pi m_0}.$$

The current strength, measured in electromagnetic units, due to the revolving electron, calculated as the quantity of electricity that passes a point per second is $-\,\mathbf{e}/T$, and the magnetic moment

μ, due to this current, calculated from the intensity of the current and the area of the circuit is :

$$\mu = -\frac{\mathbf{e}A}{T}$$

Hence,

$$\mu = -\frac{\mathbf{e}\mathrm{j}h}{4\pi m_0 c} = -\frac{\mathbf{e}\mathbf{p}}{2m_0 c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where **e** is now measured in electrostatic units, and the equation is a vectorial one. We may proceed to generalise for an atom having several electrons, by summing the contributions made by all of them, so that if $\mathrm{j}h/2\pi$ now denotes the resultant angular momentum of all the electrons, and μ the magnetic moment of the atom, we obtain an equation identical with equation (2). This theory requires, therefore, that the magnetic moments of atoms shall be multiples, or half-multiples if j is an integer plus $\frac{1}{2}$, of an elementary unit, called the *Bohr magneton*, and denoted by μ_B, given by the equation,

$$\mu_B = \frac{\mathbf{e}h}{4\pi m_0 c}.$$

Using the known values of **e**, h, m_0 and c, its value is $9{\cdot}21 \times 10^{-21}$ erg/gauss. Thus the angular momentum, measured in units $h/2\pi$, is equal to the magnetic moment, measured in Bohr magnetons, but this only applies to an atom whose Zeeman effect is normal.

The normal effect, however, is by no means the most common one encountered in spectroscopy. If a spectral line is multiple in structure, the line is termed a multiplet, and when subjected to a weak magnetic field H, each component line of the multiplet is resolved into a large number of components, whose displacements from their original frequencies are proportional to H, but different for the various members of the multiplet. As the field is gradually increased in strength, so that the displacements of the components become of the same order of magnitude as the original range of the multiplet, the resolutions undergo gradual changes, until for strong fields the components of the various members of the multiplet flow together, and produce a normal Zeeman effect. This change on passing from a weak to a strong field is known as the ***Paschen-Back effect.***

Under the influence of a magnetic field, each energy level suffers a frequency displacement, $\delta\nu$, given by :

$$\frac{\delta\nu}{o} = \mathrm{m}g,$$

where o is the normal Larmor separation, m, the magnetic quantum number which takes the values j, j $-$ 1, j $-$ 2, ... $-$ j for each j term, and g is the so-called *Landé splitting factor*. The latter may be expressed in terms of l, j and s. An empirically correct expression for g was first given by Landé, and, with the assumption that the ratio of the magnetic to the mechanical spin moment is double that for the orbital moment, it has now been deduced theoretically by means of the new mechanics. Its value is given by :

$$g = 1 + \frac{\mathrm{j}\,(\mathrm{j}+1) + \mathrm{s}\,(\mathrm{s}+1) - \mathrm{l}\,(\mathrm{l}+1)}{2\,\mathrm{j}\,(\mathrm{j}+1)},$$

and for an atom with an anomalous Zeeman effect, the factor o is replaced by go.

Now if μ_{H} is the atomic magnetic moment resolved along the magnetic field H, and $\mathrm{p_H}$, the corresponding component of the angular momentum,

$$\frac{\mu_{\mathrm{H}}}{\mathrm{p_H}} = \frac{\mu}{\mathrm{p}} = \frac{\mathrm{e}}{2m_0c}.$$

But $\mathrm{p_H} = \mathrm{m}h/2\pi$, where m is the quantum number used in the theory of the Zeeman effect, so that :

$$\mu_{\mathrm{H}} = \mathrm{m}\left(\frac{\mathrm{e}h}{4\pi m_0 c}\right).$$

Thus m denotes the angular momentum of the atom about the magnetic field in units $\frac{h}{2\pi}$ and also the magnetic moment of the atom, expressed in magnetons, for an atom with the normal

Zeeman effect. But for an atom with an anomalous Zeeman effect, *o* is replaced by *go*, where *g* is the splitting factor. Hence,

$$\mu_{\mathrm{H}} = g\mathrm{m}\left(\frac{eh}{4\pi m_0 c}\right),$$

and
$$\mathrm{p_H} = \frac{\mathrm{m}h}{2\pi},$$

so that,
$$\frac{\mu_{\mathrm{H}}}{\mathrm{p_H}} = \frac{g\mathrm{e}}{2m_0 c},$$

which agrees with experimental results for ferromagnetics if $g = 2$.

According to the new mechanics the quantum numbers have now the following meaning. In a magnetic field a single l j energy level separates into a number of component levels. They can be specified by a magnetic quantum number m, which may be regarded as the resolved value of j in the direction of the magnetic field; s is now the quantum number for the spin of the electron itself. The resolved magnetic moment of the atom, expressed in Bohr units is given by mg, and can only assume therefore certain discrete values. This supports the fact that in the Zeeman effect discrete lines are obtained.

2. The Magnetic Deflection of Atomic Rays. The presence of a magnetic field thus affects the motion of an electron, and to a close approximation, in the case of hydrogen, the plane of the electron-orbit rotates uniformly round an axis drawn through the nucleus parallel to the lines of force. The resolved component of the angular momentum must satisfy the condition, $\mathrm{p_H} = \mathrm{m}h/2\pi$, where m takes the values, o, $\pm$ 1 . . . $\pm$ j. In the case of other atoms, *e.g.*, silver, m can take the values $\pm \frac{1}{2}, \pm \frac{3}{2} \ldots \pm$ j; for such atoms j is always an integer plus one-half. Thus for atoms in a uniform magnetic field only discrete orientations are possible, such that j cos α = m where α is the angle between the magnetic field and the vector j. The atom can take up only 2j + 1 orientations in the field. In these considerations we have not taken into account the intrinsic angular momentum of the electron due to its

pin, $^{1\ h}$

This restriction of orientations was first pointed out by Sommerfeld,[*] and confirmed experimentally by Gerlach and Stern.[†] In addition, these experimenters proved that certain atoms have magnetic moments equal to the Bohr magneton. Their first experiments dealt with the magnetic moment of the silver atom in the vapour state, and later they extended the work to many other atoms and molecules.

The metal to be investigated was obtained in the form of a beam of uncharged atoms, moving in a space so highly exhausted that the atoms traverse it without a collision. The beam was formed by vaporising a metal in a very high vacuum. The atoms, shot off with a velocity which could be deduced from the kinetic theory of gases, from the temperature of vaporisation, passed through suitable slits which isolated a narrow beam.

Now a small magnet, placed in a homogeneous magnetic field, experiences no resultant force, for the force on one pole will be exactly equal, but opposite in direction, to that exerted on the other. If the field is non-homogeneous, however, the magnet will experience an acceleration. In particular, if the magnetic axes of the magnets lie parallel, or anti-parallel, to the field, the magnets whose axes are parallel to the field will tend towards one direction, and the magnets whose axes are anti-parallel will tend to move in the opposite direction. Thus in the case of a beam of atoms sent through a non-homogeneous field, in which the gradient of the magnetic force is normal to the beam, we should expect the beam to be merely broadened if, as on the classical theory, all directions of the atomic moment in the magnetic field be admitted. On the other hand, if definite directions are assumed for the atomic moments, the beam will be resolved into definite constituent beams on passage through the field, and so if the deflection of the beam can be observed, experiment will afford a decision for, or against, space quantisation. In the general case the number of parts into which the beam is split, *i.e.*, the number of orientations will be $2j + 1$. Thus, for elements in the first column of the periodic table, for which $j = \frac{1}{2}$, there should be two beams.

---

[*] *Phys. Zeits.*, 17, 491 (1916).

[†] *Ibid.*, 8, 10 (1921) : 9, 349, 3

The theory of the experiment is as follows : let μ be the magnetic moment of the atom, H the field strength, and $\frac{\partial H}{\partial x}$ the field gradient, which is in the same direction as H and normal to the path of the atom. If the magnetic axis of the atomic magnet makes an angle θ with the direction of H, the force acting on the magnet is $\mu \cos \theta \frac{\partial H}{\partial x} = \mu_{\mathrm{H}} \frac{\partial H}{\partial x}$, where μ_{H} is the component of μ, resolved along the field. If the moving atom has a velocity v and mass m_0, and traverses a path of length L, at every point of which $\frac{\partial H}{\partial x}$ has the same value, the displacement of the atom, x, normal to its direction of motion, is given by :

$$^{\omega} \; - \; 2\, m_0 \; \partial x \; \backslash v$$

If all the atoms have the same velocity, then the displacement, x, is the same for all, but actually, if they are obtained by evaporation, they will have the Maxwellian distribution of velocity, and each beam, into which the original beam is split, will be broadened out.

The velocity of the atoms depends on the temperature of vaporisation of the metal, and is given, theoretically, by :

$$\frac{1}{2} m_0 v^2 = \frac{3}{2} kT,$$

where k is Boltzmann's constant, and T, the absolute temperature ; but in the experiments the mean velocity of atoms issuing through slits was somewhat greater than this, and the average value was taken to be

$$v = \sqrt{3{\cdot}5kT/m_0}.$$

The actual apparatus used by Gerlach and Stern is shown diagrammatically in Fig. 38. The metal investigated was contained in a small furnace F, which itself was contained in a separate vessel communicating with the rest of the apparatus by the slit A, through which issued the metal atoms. The furnace vessel was exhausted, and the beam of atoms, limited by small holes in the diaphragms SS, passed between the poles of a magnet MM, which produced a non-homogeneous field, varying strongly in the vertical direction, as shown at (*a*), but uniform at all points on a given horizontal line in the diagram. The atoms were finally deposited on a glass plate G, where they formed a deposit, usually too faint to be seen, but which could be developed to good visibility. The whole apparatus of diaphragms and magnetic poles was enclosed in a vessel, which was very highly exhausted.

The essential parts of the apparatus were quite small. In some cases the pole piece was about 5 cms. long, the plate, which received the atoms, 3 mm. square, and the oven 2 cm. long. The distance between the knife edge and the plane of the slotted pole-piece was about 1 mm. The deflections obtained in the experiments were small, and careful alignment of the parts was necessary for good results. Values of $\frac{\partial H}{\partial x}$ were obtained by measuring the repulsion at various points of a thin bismuth wire, mounted parallel to the edge of the wedge. The non-homogeneity of the field is, of course, greatest in the vertical line through the edge of the wedge, and decreases to left and right, so that if the atomic beam were split into two, these two component beams would be most widely separated in this line, the separation diminishing on either side, until a place is reached where the gradient is not sufficiently strong to produce a resolution of the beam.

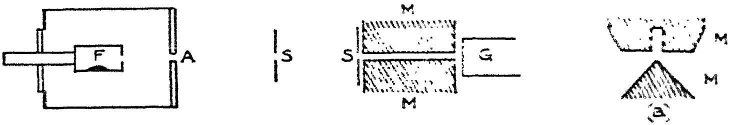


FIG. 38.—Experimental arrangement for measuring the magnetic deviation of atomic rays. (Gerlach and Stern.)

In the case of silver a splitting into two of the beam was observed, and from the measured deflection x, the value of μ_H was calculated to be ± 1 Bohr magneton. But for silver in the normal state $j = \frac{1}{2}$, and so $m = \pm \frac{1}{2}$. Thus, since $j \cos a = m$, $\cos a = \pm 1$ and $g = 2$, *i.e.*, $mg = 1, -1$.

The experimental results prove conclusively that the silver atom is space-quantised, and confirm in a striking manner the theory of the Zeeman effect. Indeed, we have here a direct proof of the existence of the energy states of the Bohr theory; until this time these states were no more than a mental picture, whose differences gave the spectral lines themselves. If the silver atom were able to assume any orientation whatever in the field, the two lines on the glass plate would be replaced by a continuous deposit, filling the entire region which these lines enclose. In fact, we should expect the densest part of the deposit to be in the centre, since the number of atoms whose axes make angles between θ and $\theta + d\theta$ with the field is nearly proportional to sin θ, and in this case a large fraction of the atoms would be oriented nearly transversely to the field and so would suffer very small deflections.

Typical values in the experiment were $H = 17{,}500$ gauss and $\frac{\partial H}{\partial x} = 236{,}000$ gauss/cm. at 0·15 mm. from the edge of the wedge. The measured magnetic moment per gram atom was 5,690 gauss. cm., whereas the calculated value of the Bohr magneton per gram atom is 5,589. The Gerlach-Stern experiment, which may be completely explained by wave mechanics, provides direct proof that both the Bohr magneton and space quantisation have a real existence.

The results of some of the experiments are shown in Fig. 39. For example, (*a*), (*b*) and (*c*) give the result of an experiment with silver, the trace of the rays both with and without the magnetic field being shown. The lack of symmetry of the lens-shaped deposit is due to the very strong magnetic-force gradient in the immediate vicinity of the knife edge.

Gerlach and Stern also investigated other metals. Copper, and gold atoms have, in the normal state, a magnetic moment $\pm$ 1 magneton, and, as in the case of silver, two deflected traces were obtained on the plate.

For the normal atoms of elements in the second column of the periodic table, including zinc, cadmium and mercury, there were no deflected traces, so that the value of mg for these atoms is zero.

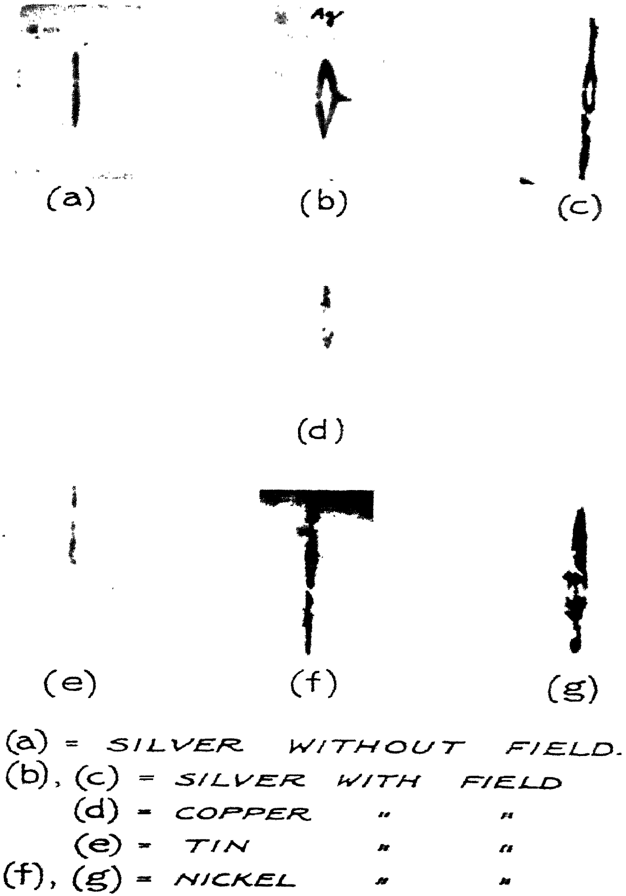


FIG. 39.—Magnetic deviation of atomic rays.

[*To face p.* 246.

Nickel showed curious results in that there were both deflected and undeflected beams. Hence some of the atoms have no magnetic moment, while others have a moment which works out to be somewhat greater than one magneton, mg being = 5 4. With antimony an undeflected beam was obtained, which was attributed to molecules. Bismuth gave two traces on the plate which were asymmetrical. Leu * repeated the experiments with bismuth, and found two broad deviated lines, separated by a narrow undeviated line which disappeared at higher temperatures. The asymmetry noted by Gerlach was not observed. The distribution of density was consistent with the presence of atoms having resolved moments in the ratio 1 : 3, the traces merging into each other. Iron has been investigated, but only an undeflected trace was obtained. Spectroscopy suggests a value of mg equal to ± 5/4, but in the actual experiments difficulties were encountered owing to the rapid oxidation of the traces on the plate. The experiments are not regarded as final. Recently Gerlach † has found that the results for iron atoms do not, as at first supposed, indicate mg = 0, but suggest that mg > 6. In the case of cobalt a value mg = 6 can just be established.

The behaviour of a diamagnetic atom, or molecule, under the conditions of the Stern-Gerlach experiment is quite different from that of the paramagnetic unit. Since the magnetic moment of the diamagnet is, except for a small correction term, directly proportional to H and anti-parallel to H, all the units of one kind should follow the same path, and no resolution into discrete beams can be expected.

Perhaps the most interesting case is that of hydrogen, which was investigated by Phipps and Taylor.‡ The beam was formed in a special all-glass slit system of three slits, sealed to a discharge tube, and detected by the reduction resulting on contact with a target coated with molybdenum trioxide. A sharply defined blue line against a white background was the result. In the magnetic field the beam was separated into two branching beams.

---

* *Zeits. f. Phys.*, **49**, 498 (1928).

† *Journ. d. Phys.*, **10**, 273 (1929).

‡ *Phys. Rev.*, **29**, 309 (1927).

There was also evidence of a central undeviated beam, which was believed to be due to hydrogen, chemically active, but not in the atomic state. From a measurement of the deflection, the magnetic moment of the hydrogen atom was calculated to be one Bohr magneton, within the limits of experimental error. This result is of interest because according to the newer quantum theory, the electric field of the hydrogen atom in the normal state possesses spherical symmetry, and must, therefore, under all circumstances, show perfect isotropy in collisions with other atoms. This leads to zero magnetic moment for the normal state, whereas experiment gives ± 1 magneton. Thus the spin of the electron must be taken into account, and that which orients in this case is, apparently, the electron momentum vector, $\frac{1}{2} \cdot \frac{h}{2\pi}$, so that the corresponding magnetic moment equals one Bohr magneton. On the whole, the determination of atomic magnetic moments, made by Gerlach and Stern, agrees very well with the deductions made from spectroscopy as regards the moments of atoms in their normal states.

So far we have not taken into account any possible moment of the atomic nucleus, but Back and Goudsmit [*] explained the hyperfine structure of the bismuth spectrum as due to very close multiplet combinations, arising from a nuclear moment, and confirmed the theory by the Zeeman effect on the bismuth lines in a strong field. The Zeeman effect observations enabled the magnitude of the mechanical moment of the nucleus to be determined. This was found to be $4 \cdot 5 \frac{h}{2\pi}$. Jackson [†] investigated the lines of the principal series of the arc spectrum of cæsium, searching for hyperfine structure due to nuclear spin. The lines were found to consist of close doublets, suggesting a nuclear spin of one half quantum. The ratio of the separation due to the nuclear spin to that due to the electron spin was calculated to be 1 : 120,000, whereas experiment gave 1 : 55,000, and the ratio of the magnetic moment of the cæsium nucleus to the moment of the electron is

[*] *Zeits. f. Phys.*, 47, 174 (1928).

[†] *Proc. Roy. Soc.*, *A*, 121, 432 (1928).

about 1 : 2,000. Taylor[*] showed that in the case of lithium a nuclear magnetic moment must be present smaller than one-third of the Bohr magneton.

The nucleus possesses a magnetic moment by virtue of being a rotating charge in the same way as the electron, considered as a point charge rotating round the nucleus, produces a magnetic field. The nucleus will therefore suffer an increase, or decrease, according to the sense of rotation, in potential energy, just as the electron does with its magnetic moment in similar circumstances. Although much work remains to be done, observations indicate that the nuclear spin, whether due to electrons, protons, or to both electrons and protons, carries with it, in space quantisation, the total mass of the nucleus. Assuming the nuclear spin to be a rotation of the nucleus as a whole, Jackson derived the following equation for the approximate shift in energy of the ordinary energy levels produced by the nuclear spin :

$$\frac{\delta\nu_g}{\delta\nu_f} = \frac{m_k}{2m_e}.$$

Here $\delta\nu_g$ is a gross, or multiplet, structure separation, $\delta\nu_f$ the corresponding hyperfine structure separation, m_e the mass of an electron, and m_k the mass of the nucleus.

Fermi[†] deduced the magnetic moments of the nuclei of sodium and cæsium atoms from the hyperfine structure of the spectra of these elements. Comparing the relative intensities of the components, he estimates the mechanical moment of the nucleus to be $h/2\pi$ for sodium. This makes the atomic magnetic moment equal to $\mu_B/670$, where μ_B is one Bohr magneton. If $h/2\pi$ is also the mechanical moment of the cæsium nucleus, $\mu_B/1460$ is its magnetic moment.

Other workers who have investigated the hyperfine structure of spectra lines include Dorfman,[‡] Güttinger,[§] McLennan and Allin,[||] Schüler and Brück,[¶] White,[**] Goudsmit and Bacher.[††]

---

[*] *Zeits. f. Phys.*, **52**, 11 (1929).

[†] *Ibid.*, **60**, 320 (1930).

[‡] *Ibid.*, **62**, 90 (1930).

[§] *Ibid.*, **64**, 749 (1930).

[||] *Proc. Roy. Soc., A*, **129**, 208 (1930).

[¶] *Zeits. f. Phys.*, **58**, 735 (1929).

[**] *Phys. Rev.*, **34**, 1397 (1929) ; **34**, 1404 (1929).

[††] *Ibid.*, **34**, 1501 (1929).

3. Diamagnetism. Diamagnetic substances are characterised by having magnetic intensity proportional, and in the opposite direction, to the magnetising field, the ratio of the intensity of magnetisation, **I**, to the magnetising force, H being the volume susceptibility, χ_v. The mass, or specific, susceptibility, χ, is given by $\chi = \chi_v/\rho$, where ρ is the density.

There is a great prevalence of diamagnetic properties among elements and compounds, about half of the elements in the periodic table being what we may term diamagnetic. By this we mean that all the saturated compounds which they form with each other are diamagnetic, although the elements themselves may show paramagnetism in the free state. In addition, even such elements as iron or nickel form many complex salts which are actually diamagnetic.

Langevin * showed that a magnetic molecule, consisting of a spherically symmetrical distribution of electrical charges, either at rest or in orbital motion, has no tendency to orient itself in any particular direction with respect to a magnetic field, but would begin to rotate with a definite angular velocity round the lines of magnetic force, the angular velocity ω, the Larmor rotation, being given by :

$$\omega = -\frac{\mathrm{e}H}{2m_0c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This result may also be stated in another way. The equations of motion of an electron, relative to fixed axes, in the absence of a magnetic field, retain, very approximately, the same form in the presence of a magnetic field, H, provided the axes are supposed to rotate with angular velocity, $\omega = \mathrm{e}H/2m_0c$, about the direction of the field. We see from this that when a magnetic field is produced in a substance in which the electrons are describing orbits in fields of force, the orbits in the field will be the same, relative to axes rotating about the direction of the field with velocity $\omega = \mathrm{e}H/2m_0c$, as they were, relative to fixed axes, before the field was applied, provided that the application of the magnetic field does not move the fields of force.

* *Ann. d. Phys.*, 5, 70 (1905).

In diamagnetic substances we suppose that the atoms have zero magnetic moments in the absence of a magnetic field, so that when a field is applied, it does not tend to move them.

Now an electron at a distance r_1 from an axis, revolving with angular velocity ω round that axis, gives rise to a magnetic moment, $\delta\mu$, in the direction of the magnetic field, where

$$\delta\mu = \frac{\mathbf{e}}{c} \cdot \frac{\omega}{2\pi} \pi r_1^2 = \frac{\mathbf{e}\omega r_1^2}{2c}.$$

or, from equation (3),

$$\delta\mu = -\frac{\mathbf{e}}{4m_0c^2} \mathbf{e}r_1^2 H.$$

where $\mathbf{e}$ is measured in electrostatic units, and the negative sign is correct, because an increasing magnetic field tends to induce currents which produce a field, opposite in direction to the inducing field. Hence the electrons in orbits which give a field opposite to the field H will be accelerated, and the electrons in orbits giving a field in the same direction will be retarded.

If the atom contains several electrons, the total magnetic moment, $\Delta\mu$, of the atom is given by :

$$\Delta\mu = -\frac{\mathbf{e}}{4m_0c^2} \sum \mathbf{e}\overline{r_1^2} H.$$

where the summation sign refers to different orbits in the same atom, and $\overline{r_1^2}$ is the mean value of r_1^2 for a single orbit.

Owing to the spherical symmetry of the diamagnetic atom, we have :

$$\sum \mathbf{e}\overline{r_1^2} = \frac{2}{3} \sum \mathbf{e}\overline{r^2},$$

where r_1 refers to the distance of the typical electron from the axis of rotation through the nucleus, and r refers to its distance from the nucleus itself. Thus,

$$\Delta\mu = -\frac{\mathbf{e}}{6m_0c^2} \sum \mathbf{e}\overline{r^2} H.$$

The magnetic moment per gram-atom is, therefore,

$$\Delta\mu_{\text{A}} = -N\frac{\mathbf{e}}{6m_0c^2} \sum \mathbf{e}\overline{r^2} H,$$

where N is Avogadro's number, 6·06 × 10^{23} atoms per gram-atom. **I**, the magnetic moment per unit volume, or intensity of magnetisation, is given by :

$$\mathbf{I} = \Delta\mu_v = - N\frac{\rho}{\mathrm{A}}\,\frac{\mathrm{e}}{6m_0c^2}\sum\mathrm{e}\overline{r^2}H,$$

where ρ is the density of the substance and A, its atomic weight.

The *volume susceptibility*, χ_v, is therefore,

$$\chi_v = \frac{\mathbf{I}}{H} = - N\frac{\rho}{\mathrm{A}}\cdot\frac{\mathrm{e}}{6m_0c^2}\sum\mathrm{e}\overline{r^2}.$$

The *atomic susceptibility*, or susceptibility which the substance would possess if one gram-atom of it were concentrated in unit volume, is thus :

$$\chi_{\mathrm{A}} = \frac{\Delta\mu_{\mathrm{A}}}{H} = - N\frac{\mathrm{e}}{6m_0c^2}\sum\mathrm{e}\overline{r^2}.$$

Another constant often used in defining susceptibility is the *mass*, or *specific*, *susceptibility*, χ, and,

$$\chi = -\frac{N}{\mathrm{A}}\,\frac{\mathrm{e}}{6m_0c^2}\sum\mathrm{e}\overline{r^2}.$$

Substituting numerical values :

$$\chi_{\mathrm{A}} = - 2{\cdot}85 \times 10^{10}\sum\overline{r^2} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If we suppose that the substance considered contains free electrons, moving about inside it like the molecules of a gas, then these electrons will also produce a small diamagnetic susceptibility. The theory of this effect was given by Schrödinger, and later by Wilson,* in a simpler form. The volume susceptibility, χ_e, due to the electrons, is shown to be :

$$\chi_e = -\frac{1}{3}\,\frac{n\mathrm{e}^2\lambda^2}{m_0},$$

where n is the number of free electrons per unit volume, and λ, the electronic mean free path. The diamagnetic susceptibility due to the free electrons may be of the same order of magnitude as that due to the electrons describing orbits, but there is no way of estimating the relative values of the two.

---

* *Proc. Roy. Soc.*, *A*, **97**, 321 (1920).

The above expressions for susceptibilities are independent of the temperature, and also of the field strength. They hold for the quantum orbital model of the atom, and are of direct importance only for atoms, or ions, with no resultant moment. In addition, the theory outlined above only applies to such systems as atoms, or to ions in solution or solids, where we may regard the atoms, or ions, as independent. For molecules, *i.e.*, systems with more than one centre of force, $\overline{r^2}$ loses its simple significance.

A number of accurate measurements of the susceptibilities of alkaline and alkaline earth halides are now available, and these give values of $\overline{r^2}$ compatible with other evidence. The susceptibility increases fairly regularly in a series such as Na^-, K^-, Rb^-, F^-, Cl^-, Br^-. For ions with the same number of electrons the susceptibility decreases as the nuclear charge increases, as in Cl^-, K^+, Ca^{++}. Earlier measurements suggested that the inert gases were anomalous, but the measurements of Wills and Hector * show that they fall into line, Ar for example, falling between Cl^- and K^+.

If the orbital model is replaced by the space charge model, it is possible to calculate the equivalent value of $\overline{r^2}$ from the distributions for symmetrical ions.† The agreement with experiment is good for the inert gases and positive ions, but there are considerable discrepancies for the negative ions.

It may be noted that the orbital model gives values which are too great in cases where approximately complete calculations can be made, namely, for He and H. It was shown by Van Vleck,‡ however, that the new mechanics leads to satisfactory values. He has extended the treatment to the hydrogen molecule, and the agreement with experiment is very satisfactory.

4. Experimental Results. In dealing with experimental results for material in bulk, it is convenient to consider first those from which values for quasi-independent ions, or atoms, can be deduced with the minimum of uncertainty. The ideal substances are monatomic gases; but fairly definite conclusions can also be drawn from solutions of salts, containing definite ions, and from solid salts which are definitely ionic.

---

* *Phys. Rev.*, **24**, 418 (1924).

† See Stoner, *Proc. Leeds Phil. Soc.*, **1**, 484 (1929).

‡ *Proc. Nat. Acad. Sci.*, **12**, 662 (1926); *Phys. Rev.*, **31**, 587 (1928).

The electronic structure of the inert gases has long been known to possess a very high degree of symmetry, and it is naturally to them that one would turn first to test a theory of diamagnetism, based on electrical symmetry. The first definite attempt to apply the theory to the diamagnetism of the rare gases seems to have been that of Pauli.* He calculated a value of $\sum e\overline{r^2}$ for argon and helium, and proved definitely that the experimental results of Tänzler † and Také Soné ‡ indicated an atomic susceptibility far greater than any reasonable theory would allow. The very careful measurements of Hector,§ using a sensitive magnetic balance method developed by Wills,‖ have shown that Pauli's deductions were correct, and that the atomic susceptibilities of the inert gases are only about one-tenth of the values found previously. Hector's results were as follows:

SUSCEPTIBILITY OF INERT GASES.

Element.	$-\chi_v \times 10^{10}$.	$-\chi_a \times 10^6$.	$\Sigma e\overline{r^2} \times 10^{26}$.
Helium . .	0·780	1·87	3·14
Neon . .	2·77	6·62	11·1
Argon. . .	7·52	18·0	30·2

Other three configurations of almost equal importance in a consideration of the periodic table have no resultant magnetic moment, namely, those of the ions Cu^+, Ag^+ and Au^+. Of these, Ag^+ is definitely stable under the attraction of a nuclear charge of $+47$, as the strictly monovalent character of silver, and the lack of colour in its simple salts indicate. The distributions of electrons, according to Pauli's theory, in the Cu^+ and Au^+ ions seem to be capable of existence under nuclear charges + 29 and + 79, respectively, but the fact that Cu^{++} and Au^{+++} occur more often in combination, proves that these distributions are not stable. Spectroscopic considerations point to exactly the same conclusion.[*]

---

* *Zeits. f. Phys.*, **2**, 201 (1920).

† *Ann. d. Phys.*, **24**, 931 (1907).

‡ *Phil. Mag.*, **39**, 305 (1920).

§ *Phys. Rev.* **24**, 418 (1924).

‖ *Ibid.*, **23**, 209 (1924).

The theory of diamagnetism has been abundantly tested in the case of ions in solutions and in salt crystals. Joos[†] was the first to apply the theory to solutions of the alkali halides. In solution these salts are dissociated into alkali ions with a single positive charge, and halogen ions with a single negative charge. The ions possess exactly the same number of electrons as members of the inert gas series, and, presumably, the same electronic configuration. To take a concrete case, a solution of KCl will contain K^+ ions and Cl^- ions, both with eighteen electrons, the same number as in the inert gas argon, which falls between chlorine and potassium in the periodic table. Owing to its larger nuclear charge, + 19, the K^+ ion will be smaller than the Cl^- ion with nuclear charge + 17. Joos makes the assumption that the linear dimensions of the electronic system are inversely proportional to the nuclear charge, and that the susceptibility is, therefore, inversely as the square of the charge.

More recently, Ikenmeyer,[‡] a differential method, measured the effect of a non-homogeneous magnetic field on a rod suspended in an aqueous solution of the salt under test. He found that the susceptibility of the solution is a linear function of the concentration within the range of the investigation. It follows that there is no perceptible mutual action between the ions in the solution, and his results showed that :

$$\chi = C_s \chi_s + (1 - C_s)\, \chi_w,$$

where χ, χ_s and χ_w are the susceptibilities of the solution, salt and water, respectively, and C_s is the concentration of the salt. Values were found for the molecular susceptibilities of the twenty salts investigated, and these gave an approximately linear function when plotted against the sum of the nuclear charges of the ions forming the molecule. From these results an estimation was made of the relative contributions of the anion and kation to the susceptibility of one particular salt, in a manner similar to that made by Joos, and a series of ionic susceptibilities was determined by comparing different salts containing the same anion or kation. His results for the molecular susceptibilities of different salts are given in Table VII.

---

[*] See Grimm and Sommerfeld, *Zeits. f. Phys.*, 36, 36 (1926).

[†] *Ibid.*, 19, 347 (1923) ; 32, 835 (1925).

[‡] *Ann. d. Phys.*, 1, 169 (1929).

TABLE VII. MOLECULAR SUSCEPTIBILITIES (χ_M).

Salt.	$\chi_M \times 10^6$.	Salt.	$\chi_M \times 10^6$.	Salt.	$\chi_M \times 10^6$.
LiCl	—24·4	RbBr	—66·1	$CaCl_2$	— 51·7
NaCl	—30·8	LiI	—53·3	$SrCl_2$	— 66·1
KCl	—37·2	NaI	—59·7	$BaCl_2$	— 80·6
LiBr	—38·8	KI	—66·1	$MgBr_2$	— 74·1
NaBr	—45·2	CsI	—95·0	$SrBr_2$	— 95·0
KBr	—51·7	$MgCl_2$	—45·2	$BaBr_2$	—109·5

Taking $\chi = -95{\cdot}0 \times 10^{-6}$ for cæsium iodide, Ikenmeyer found the relative susceptibility contributions of the anion and kation to be:

$$Cs^+ = -45{\cdot}75 \times 10^{-6},$$
$$I^- = -49{\cdot}25 \times 10^{-6}.$$

From the values of the molecular susceptibilities, given in Table VII, and the values of the gram-ion susceptibility, χ_i, of the Cs^+ and I^- ions, he derived the gram-ion susceptibility of other ions, the results being shown in Table VIII.

TABLE VIII. SUSCEPTIBILITY PER GRAM-ION ($\chi_i \times 10^6$).

Ion.	$\chi_i \times 10^6$.	Ion.	$\chi_i \times 10^6$.	Ion.	$\chi_i \times 10^6$.
F^-	(—13·9)	Li^+	— 4·0	Mg^{++}	— 4·5
Cl^-	—20·4	Na^+	—10·4	Ca^{++}	—11·0
Br^-	—34·8	K^+	—16·9	Sr^{++}	—25·4
I^-	—49·25	Rb^+	—31·3	Ba^{++}	—39·9
		Cs^+	—45·75		

If the molecular susceptibility, χ_M, of a salt is plotted against the sum of the atomic numbers of the constituents, Z_M, a linear relationship is obtained, which may be represented by:

$$-\chi_M = c_1 Z_M + c_2,$$

where $c_1 = 0{\cdot}80 \times 10^{-6}$ and $c_2 = 8{\cdot}30 \times 10^{-6}$.

In a similar manner the relationship between the gram-ion susceptibility, χ_i, and the atomic number, Z, of the ion is, from the curves relating χ_i and Z,

$$-\chi_i = c_1 Z + c_2',$$

$c_2' \times 10^6$ for the halogen, alkali and alkaline earth ions being 6·7, 1·60 and — 5·1, respectively, and c_1, the same for the different series of ions. Thus, to a first approximation, the mean square of the electronic path radius, $\overline{r^2}$, is independent of the number of electrons, and a numerical calculation gives $\overline{r^2} = (0{\cdot}531 \times 10^{-8})^2$, the quantity in brackets being the radius a_0 of the innermost orbit in the Bohr hydrogen atom. This average value of $\overline{r^2}$ is of the right order, since atomic radii are, in general, small multiples of 10^{-8} cm. In the case of the same electronic configuration, *e.g.*, K^+, A, Cl^-, there should be a decrease in size, and hence in susceptibility, with increasing nuclear charge. This is so for these three elements:

$$\begin{aligned} K^+,\ \chi_i &= -16{\cdot}9 \times 10^{-6}, \\ A,\ \chi_i &= -18{\cdot}0 \times 10^{-6}, \\ Cl^-,\ \chi_i &= -20{\cdot}4 \times 10^{-6}. \end{aligned}$$

According to the orbital theory, the mean value of r^2 for an n, k, orbit is:

$$\overline{r^2} = a_0{}^2 n^2 \left(\frac{5}{2} n^2 - \frac{3}{2} k^2\right),$$

where a_0 equals $h^2/4\pi^2 m_0 Ze^2$, the radius of a one-quantum orbit, *i.e.*, the innermost orbit in the hydrogen atom. Thus the contribution which this orbit (n, k) makes to the atomic susceptibility, χ_A, is:

$$-2{\cdot}85 \times 10^{10}\, a_0{}^2,$$

or, putting in numerical values for a_0,

$$-0{\cdot}81 \times 10^{-6} \frac{n^2}{Z^2} \left(\frac{5}{2} n^2 - \frac{3}{2} k^2\right) \quad . \quad . \quad . \quad . \quad (5)$$

Van Vleck,[*] using the new quantum mechanics, finds that,

from which the susceptibility per gram-atom is :

$$= -0{\cdot}81 \times 10^{-6} \sum \frac{n^2}{Z^2}\left(\frac{5}{2}n^2 - \frac{3\,l\,(l+1)-1}{}\right) \quad . \quad (7)$$

Pauling [†] also deduced an expression for the atomic susceptibility from the wave mechanics theory, introducing a screening constant S, defined by the equation :

$$Z' = Z - S,$$

where $Z'e$ is the effective nuclear charge, and Ze the true nuclear charge. This screening constant is qualitatively explained as due to the action of electrons which are nearer the nucleus than the electron under consideration, and which, in effect, partially neutralise the nuclear field. Pauling deduced the formula :

$$\chi_A = -0{\cdot}804 \times 10^{-6} \sum \frac{n^2}{(Z-S)^2}\left(\frac{5}{2} - \qquad 2\right.$$

His calculated values for the rare gases agree fairly well with the experimentally determined values, thus :

Gas.	Helium.	Neon.	Argon.
Calculated $\chi_A \times 10^6$.	— 1·54	— 5·7	— 21·5
Observed $\chi_A \times 10^6$.	— 1·87	— 6·62	— 18·0

In addition, Pauling calculated the susceptibility of various ions. For helium-, neon-, and argon-like ions, as well as for the cuprous ion, the agreement with his predicted values is satisfactory, but for the more complicated ions the experimental values are low.

Stoner,[‡] using Hartree's [§] method of determining how the charge per unit radial distance varies with the distance from the nucleus, has calculated the diamagnetic susceptibility of ions. The results, calculated by Pauling and Stoner, together with experimental values,[‖] are given in Table IX.

---

[*] *Proc. Nat. Acad. Sci.*, 12, 662 (1926).

[†] *Proc. Roy. Soc.*, *A*, 114, 181 (1927).

[‡] *Proc. Leeds Phil. Soc.*, 1, 484 (1929).

[§] *Proc. Camb. Phil. Soc.*, 24, 89 (1928).

[‖] See Weiss, *Journ. d. Phys.*, 1, 185 (1930).

TABLE IX. CALCULATED AND OBSERVED IONIC SUSCEPTIBILITIES — $\chi_i \times 10^6$.

Ion.	Calculated Values.		Experimental Values.			
	Pauli.	Stoner.	Hogart.	Reicheneder.	Pascal.	Ikenmeyer.
Cl^-	29	40·39	23·1 ± 0·6	23·0	23·1	20·4
Br^-	54	—	33·9 ± 1·2	33·6	34·7	34·8
I^-	80	—	49·5 ± 1·7	51·3	49·8	49·25
Na^+	4·2	5·47	8·2 ± 0·9	—	7·6	10·4
K^+	16·7	17·64	16·5 ± 0·9	—	16·0	16·9
Rb^+	35	30·12	—	—	24·3	31·3
Cs^+	55	—	—	—	38·0	45·75
Mg^{++}	3·2	—	5·15 ± 2·6	—	8·0	4·5
Ca^{++}	13·3	—	10·6 ± 1·8	—	12·2	11·0
Sr^{++}	28	—	18·9 ± 1·6	—	20·6	25·4

Weiss * used the results of Hogart for NaCl and KCl, when in solution and when crystalline, and the values of the refraction of ions obtained by Fajans and Joos,† to provide a means of deducing the changes of diamagnetism and refraction brought about by solution. He deduced that the hydrogen ion H^+ in solution was paramagnetic, $\chi_{H^+} = 1{\cdot}1 \times 10^{-6}$, whereas Reicheneder ‡ had assumed its susceptibility to be zero.

The agreement between the theoretical and experimental results indicates that we are justified in assuming that every electronic orbit is acted upon by the magnetic field in the sense of change of velocity of the electron, and so takes part in the diamagnetic effect. In other words, diamagnetism is a universal property which, in the case of strongly paramagnetic bodies, is masked by the superposition of the much greater paramagnetic susceptibility.

5. Diamagnetism of Molecules. We may regard the susceptibility of a molecule as the sum of the effects of the various electronic orbits associated with each nucleus, or as the sum of the atomic susceptibilities, modified according to the manner in which the atoms are bound together to form the molecule. Hammar [*] showed that the volume susceptibility of a gas—air, oxygen, nitrogen, carbon dioxide and hydrogen—is directly proportional to its pressure. Glaser [†] found that this relationship failed at low pressures, but Lehrer's results [‡] agree with those of Hammar.

---

* *Loc. cit.*

† *Phys. Zeits.*, 19, 374 (1923); 32, 835 (1925).

‡ *Ann. d. Phys.*, 3, 58 (1929).

It is usually easy formally to represent a diamagnetic molecule as derived from a neutral group of ions—that is, a group of positive and negative ions, for which the algebraic sum of the charges is zero. We can then consider the diamagnetic changes brought about by the approach of the widely separated ions of the neutral group, first to form the molecule, and afterwards, by an imaginary forced merging of the ionic nuclei, to form a single so-called merger atom. For example, the neutral group $K^+ + Cl^-$ gives the molecule KCl and the merger atom Kr. In the formation of the molecule from the ionic group, owing to the three nuclei, there should be a decrease in the diamagnetism, and the diamagnetism of the merger atom should be less than that of the molecule, due entirely to the increased nuclear charge. This presupposes that the electrons are the same in number, configuration and quantisation. For example, assuming that the ionic susceptibility of H^+ is zero, and taking that of N^{---} to be -22×10^{-6}, the molecular susceptibility of NH_3, *i.e.*, $3H^+ + N^{---}$ is -22×10^{-6}, whereas the experimental value is $-17{\cdot}05 \times 10^{-6}$, and that of the merger atom, Ne, $-5{\cdot}7 \times 10^{-6}$. The electrons in N^{---} and Ne are the same in number, configuration and quantisation. The loss of diamagnetic susceptibility when the two ions form the neutral group is due, not only to the increased nuclear charge, but also, in part, to the development of a weak form of paramagnetism. For further examples the reader is advised to consult a paper by Gray and Farquharson.[§]

6. Diamagnetic Crystals. Several investigators [||] have shown that when one half of a single crystal of bismuth is allowed to crystallise in a strong magnetic field, different orientations are

---

, Sci., 12, 554 (

[†] *Ann. d. Phys.*, 75, 459 (1924).

[‡] *Zeits. f. Phys.*, 73, 155 (1926).

[§] *Phil. Mag.*, 10, 191 (1930).

[||] See Goetz, *Phys. Rev.*, 35, 193 (1930).

affected in different ways. The effects are a maximum if the principal axis is perpendicular to the field, and a minimum if the axis is parallel to the field. This at once leads to the conclusion that, if the susceptibility is a contributory factor in the effect, it must also have a maximum value perpendicular to the main axis and a minimum parallel to it. Nusbaum [*] has found that the mass susceptibility, χ, for bismuth, in a direction parallel to the principal axis is $-1{\cdot}13 \times 10^{-6}$ and in a perpendicular direction, $-1{\cdot}32 \times 10^{-6}$. Corresponding values for antimony are $-0{\cdot}497 \times 10^{-6}$ and $-1{\cdot}38 \times 10^{-6}$, respectively.

Several other investigators have shown that the susceptibility varies with the direction in a crystal, *e.g.*, Focke [†] with bismuth, McLennan and Cohen [‡] with bismuth and antimony, McLennan, Ruedy and Cohen [§] with zinc and cadmium, Raman with graphite. In the latter case the diamagnetic susceptibility normal to the plane of the ring is -18×10^{-6}, whilst in the plane of the ring it is -2×10^{-6}. The value can be decreased to that for sugar charcoal by powdering the graphite, in other words, particle size determines the magnetic susceptibility of graphite. Haas and van Alphen's [¶] results show that the susceptibility of bismuth at low temperatures (liquid hydrogen) is a periodic function of the field. The susceptibility in directions perpendicular to the principal axes is a complicated function of the field and of the angle between the binary axes and the field.

7. Diamagnetism in the Paramagnetic Elements. It has long been known that compounds of some paramagnetic elements occasionally show diamagnetic quality, especially Fe, Co, Ni, Pt and Pd. Welo and Baudisch [**] carried out accurate determinations of the susceptibility of specially prepared samples of complex salts containing iron, and found a number of them diamagnetic. They suggested that the diamagnetism of these salts is due to the fact that the atoms of paramagnetic elements

d., 29, 905 (1927).

[†] *Ibid.*, **36**, 319 (1930)

[‡] *Roy. Soc. Canada, Trans.*, **23**, 159 (1929).

[§] *Proc. Roy. Soc.*, *A*, **121**, 9 (1928).

[||] *Proc. Phys. Soc.*, **42**, 309 (1930)

[¶] K. Akad. Amsterdam, *Proc.*, **33**, 1106 (1930).

[**] *Nature*, **116**, 606 (1925).

have gained a sufficient number of electrons from neighbouring atoms, by sharing and transfer, to attain the electronic configuration of a rare gas. For example, potassium ferrocyanide $K_4Fe(CN)_6$ has long been known to be diamagnetic. Now each univalent atom of K will contribute one electron to the iron atom by transfer. Each CN group will add one electron by sharing. The electronic structure of the iron atom, originally with 26 electrons, thus gains 10 electrons and assumes the structure of the rare gas krypton with 36 electrons.

Co and Ni are also shown to assume the electronic structure of Kr in the diamagnetic compounds which they form. Welo and Baudisch extended their theory to explain the paramagnetic quality of certain other complex salts.

Although the main lines of the theoretical treatment of diamagnetism are clear, there are several points to be explained, and many more experimental results are required. For example, there are very few accurate measurements of the variation of susceptibility with change of state or change of structure, or of the difference between the susceptibility of an ion in solution and in solids.

8. Paramagnetism. The magnetic moment of an atom is the vector sum of the moments of its electron orbits and spinning electrons. If this is zero in the absence of an applied magnetic field, the atom is diamagnetic, but if it is not zero the atom is paramagnetic, and tends to turn so as to set the axis of the resultant magnetic moment parallel to the magnetic field. Thus the intensity of magnetisation of the substance, composed of such atoms, is increased. The effect of the magnetic field on the electron orbits, which produce diamagnetism, must also occur in paramagnetic substances, but it is usually far too small to be appreciable, compared with the paramagnetic effect of the permanent moments of the atoms.

A theory of the paramagnetism of gases and liquids was first derived by Langevin,* on the assumption that the molecules of a gas were small permanent magnets, without transverse dimensions, so that the principal moment of inertia about the magnetic axis of each was zero. The treatment was classical, and it was assumed that all magnetic states—all relative orientations of a magnet and the applied magnetic field—were permissible. The temperature dependence of paramagnetic susceptibility arises, on this theory, from the increasing number of collisions with increasing temperature at constant volume. The equation deduced by Langevin and known as Langevin's function is :

---

* *Ann. Chim. Phys.*, 5, 70 (1905).

$$\frac{\mathbf{I}}{\mathbf{I}_s} = \coth\frac{\mu H}{kT} - \frac{kT}{\mu H},$$

where **I** is the intensity of magnetisation per unit volume, $\mathbf{I}_s$, the saturation value of **I**, *i.e.*, all the molecules in alignment with the magnetising field, μ, the magnetic moment per molecule and k, the gas constant for one molecule. When $\mu H/kT$ is small, as is usually the case,

$$\coth\frac{\mu H}{kT} - \frac{kT}{\mu H} = \frac{\mu H}{3kT},$$

and $$\frac{\mathbf{I}}{\mathbf{I}_s} = \frac{\mu H}{3kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If n_v be the number of molecules per unit volume, n_m, the number per unit mass and n_M, the number per gram-molecule, then $\mathbf{I}_s = n_v\mu$, and χ_v, the *volume susceptibility*, is given by :

$$\chi_v = \frac{\mathbf{I}}{H} = \frac{n_v\mu^2}{3kT}.$$

The *mass susceptibility*, χ, is :

$$\chi = \frac{n_m}{n_v}\chi_v = \frac{n_m\mu^2}{3kT} = \frac{C}{T},$$

while the *susceptibility per gram-molecule*, χ_M, is :

$$\chi_M = \frac{{}^{,2}}{3kT} = \frac{\sigma_{-}{}^{2}}{3RT},$$

where $n_M k = R$, the gas constant per gram-molecule, and the saturation value of the magnetic moment per gram-molecule. This last equation, known as Curie's law, is usually written :

$$\chi_M = \frac{C_M}{T},$$

where $C_M = \frac{\sigma_0^2}{3R}$ is *Curie's molecular constant*. Thus, for a paramagnetic substance which rigidly obeys Curie's law, a single determination of χ_M gives the saturation value, σ_0, per gram-molecule.

The substitutes for Langevin's theory, which are acceptable in quantum mechanics, differ from it principally under extreme conditions. The new expression for relative intensity of magnetisation in terms of the saturation value :

$$\frac{\mathbf{I}}{\mathbf{I}_s} = \tanh \frac{\mu H}{kT},$$

can hardly be distinguished for wide ranges of H and T from Langevin's expression. Schidhof * has recently discussed the range of validity of the quantum result, and shows that it is not applicable near $T = 0$.

Langevin's theory predicts that in weak magnetic fields paramagnetic susceptibilities should vary inversely as the absolute temperature. This agreed with the previous experiments of Curie upon what he regarded as typical paramagnetic substances. As data accumulated, it became apparent that many paramagnetic crystals, and crystal aggregates, show a more complicated dependence upon temperature, while in other cases the paramagnetic susceptibility does not vary with temperature to any appreciable extent.† Weiss pointed out that the form of Curie's law could, at least in many cases, be preserved by measuring temperature, not from absolute zero, but from an origin chosen to give the best fit with the data. In the case of media which, at low temperatures, are ferromagnetic, this arbitrary origin, as derived from high-temperature paramagnetism, agrees fairly well with the temperature at which the ferromagnetism disappears on heating, *i.e.*, the ferromagnetic Curie point. It is therefore customary to describe the temperature at which the value of the paramagnetic susceptibility, extrapolated from higher temperatures, would become infinite, as the paramagnetic Curie point. The discrepancies between ferromagnetic and paramagnetic Curie points have been discussed by Forrer.*

---

* *Helv. Phys. Acta*, **1**, 578, 601 (1928).

† See Collet, *Comptes Rendus*, **183**, 1031 (1926) ; *Trans. Amer. Electroc. Soc.*, **55**, 79 (1929) ; Holgersson and Serres, *Comptes Rendus*, **191**, 35 (1930).

Weiss † assumed that within a magnetic body there exists a *molecular field*, produced at any point by all the molecules in the neighbourhood of that point. This field, H_0, is assumed proportional to the intensity of magnetisation, *i.e.*,

$$H_0 = \alpha \mathbf{I}.$$

The total field, H, is thus composed of the internal field H_0, and the applied field H_A, or,

$$H = H_A + H_0.$$

Hence from equation (8),

$$\frac{\mathbf{I}}{\mathbf{I}_s} = \frac{\mu(H_A + \alpha \mathbf{I})}{3kT}$$

If ρ is the density and M, the molecular weight of the substance, $\mathbf{I} = \rho\sigma/M$, where σ is the gram-molecular moment, and so,

$$\frac{\sigma}{\sigma_0} = \frac{\sigma_0}{3RT}\left(H_A + \frac{\alpha\rho\sigma}{M}\right).$$

and $$\chi_M = \frac{\sigma}{H_A} = \frac{{\sigma_0}^2}{3R(T-\theta)} = \frac{C_M}{T-\theta} \quad . \quad . \quad . \quad . \quad (9)$$

where $$\theta = \frac{\alpha\rho{\sigma_0}^2}{3RM} = \frac{\alpha\rho}{M} C_M.$$

Equation (9) which may also be written in the form : $\chi = C/(T-\theta)$, is known as the Curie-Weiss law θ being the *Curie temperature*, or *Curie point*.

Unfortunately for the simplicity of the Curie-Weiss law, the paramagnetic Curie point is often below absolute zero, and even when it lies high enough to be accessible, it is found that the law of variation of susceptibility changes as the critical temperature is approached, most substances remaining merely paramagnetic however much they may be cooled.‡ The linear relationship between $1/\chi$ and T generally breaks down. Weiss interprets such results as indicating allotropic modifications at definite temperatures, the low-temperature modification possessing a paramagnetic Curie point, different from that of the high temperature form—lower if ferromagnetism is successfully evaded. Others prefer to regard these results as proving that the simple inverse proportionality of atomic susceptibility and corrected temperature is an approximation at the best, which diverges more and more from the facts as the system becomes more and more degenerate, *i.e.*, less and less classical, with decreasing temperature. Schidlof[*] has proposed equations, which predict that at very low temperatures, the magnetic susceptibility should increase very slowly, by only one-third of its value—supposed finite—at the pseudo Curie point—here always positive—in passing from that temperature to absolute zero.

---

* *Journ. d. Phys.*, **1**, 49 (1930) ; *Comptes Rendus*, **191**, 1046 (1930).

† *Comptes Rendus*, **156**, 1674 (1913).

‡ See Woltjer and Wiersma, *Proc. Akad. Amsterdam*, **32**, 735

In crystals which do not belong to the cubic system the susceptibility varies in different crystallographic directions, and the change of susceptibility with temperature also depends upon the direction, so that one crystal may have several paramagnetic Curie points and several Curie constants, according to its orientation in the magnetic field. This suggests very forcibly that whatever these characteristic quantities really represent, they depend in some way upon the usual (most stable) orientations of the unitary magnet within the crystal. These, in turn, must be fixed by the mutual effect of adjacent atoms in that systematic arrangement which distinguishes crystals from fluids. As regards paramagnetic, as distinct from ferromagnetic, crystals, theory has made but little progress in the analysis of these effects.

Since paramagnetic effects must cease to be apparent when all the unitary magnets are co-directed, while diamagnetic effects depend directly upon the applied field intensity, up to the maximum intensities yet available, it is apparent that at a sufficiently high field intensity all paramagnetics should become diamagnetic. Such transitions have been observed[†] in the case of alloys, which are however only feebly paramagnetic.

---

[*] *Loc. cit.*

[†] See Overbeck, *Ann. d. Phys.*, 46, 677 (1915).

Langevin's theory of paramagnetism, long recognised as insufficient, has been replaced by a more general treatment due to Cabrera.[*] He obtains Langevin's formula from the following hypotheses: (*a*) the electronic configurations which belong to the more superficial layers of the atom are thrown out of order each time the atoms come within a certain distance of each other; (*b*) the reorganisation takes place in such a way as to conserve the magnetic moment; in the case where there is an external field, the probability of each orientation of the magnetic axis depends on the field, and on the action of neighbouring atoms.

For the paramagnetism of metals no theory existed until Pauli explained it as due to the spin of the free electrons, contained in the metal (Section 9, Chapter II). A more exact expression for the volume susceptibility of metals is,

$$\chi_\nu = \chi_0 + \frac{(8\pi^2 k)^2}{3^3 h^6} \cdot \frac{m^3 \mu^2}{n} \cdot T^2 = \chi_0 + \frac{T^2}{n} \cdot 10^7.$$

where

$$\chi_0 = 12\mu^2 n^{\frac{1}{3}} \frac{m}{h^2} \left(\frac{\pi}{3}\right)^{\frac{2}{3}}.$$

As n is of the order of 10^{22} (atoms per cubic centimetre), it becomes evident that the influence of the temperature is negligibly small. There is, indeed, no other property of the metal which is so independent of temperature as its magnetic susceptibility. Thus it would seem that some measurements, which have given a change in susceptibility with temperature, *viz.*, aluminium, manganese, *etc.*, require to be verified.

Pauli,[†] and later Sommerfeld,[‡] neglected the presence in the metal of the remainder of the atoms, but the free electrons must interact to some extent with the ions, and in a complete theory this interaction will have to be taken into account.

9. The Magneton. Weiss contended that whenever we can determine directly, or indirectly, the magnetic moment of an atom, this moment is found to be a whole multiple of a single elementary magnet, *the magneton.* The elementary moment per gram-atom is 1123·5 gauss-cm., corresponding to a value for the unit magnetic moment per atom, *i.e.*, the magneton, of $1{\cdot}85 \times 10^{-21}$ gauss-cm.

---

[*] *Journ. d. Phys.*, **8**, 257 (1927).

[†] *Zeits. f. Phys.*, **41**, 81 (1927).

Ibid., **47**, 1 (1928).

Since

$$C_M = \frac{\sigma_0{}^2}{3R},$$

the magnetic moment per gram-molecule can be calculated from the value of Curie's constant, and is usually expressed as p Weiss magnetons. Thus :

$$p = \frac{\sigma_0}{1123{\cdot}5} = 14{\cdot}07\ C_M{}^{\frac{1}{2}}.$$

To determine the value of C_M, it is not necessary, in practice, to produce saturation conditions, which are, in fact, very difficult to obtain. We may, for example, measure the susceptibility at very low temperatures. With ferromagnetics, the susceptibility may be determined at temperatures well above the Curie point, when the substance becomes paramagnetic. At such temperatures

$$\chi_M = \frac{C_M}{T - \theta}.$$

Then again, we may use solutions of paramagnetic salts, and from the formula :

$$\chi = \frac{C_M}{T},$$

determine the value of C_M.

A fixed number of magnetons is not, however, invariably associated with an atom of a given element. Thus when $\dfrac{1}{\chi_M}$ is plotted against T for a ferromagnetic substance above the Curie point, the curve consists of a series of straight lines of different slopes, which suggests that if we admit the idea of the Weiss magneton the number of magnetons associated with a given kind of atom changes abruptly at different temperatures. Also, in the case of solutions, the number of magnetons associated with a given atom depends on the valency of the salt in solution. Metallic nickel, for example, has three magnetons at temperatures near the absolute zero, eight at temperatures 500° C.—900° C., and nine above 900° C. Combined as a salt, it can have either fifteen or sixteen magnetons in the solid state, and sixteen in solutions. In other cases variations from a whole number of magnetons are found.

From the simple Bohr orbital theory for the unit quantum state, the value of the magneton is 5,589 gauss-cm. per gram-atom, a value which is almost exactly five times that of the Weiss magneton, but here, again, the number of Bohr magnetons found experimentally for different atoms are seldom multiples of 5. The infrequent occurrence of multiples of 5 Weiss magnetons, however, can be explained on the quantum theory as follows :

According to the classical theory any orientation of the elementary magnet is possible, but on the quantum theory the orientations are quantised. Now, in the equation :

$$\chi_M = \frac{\sigma_0{}^2}{3RT}.$$

the factor $\frac{1}{3}$ is the result of taking the average value of $\cos^2\phi$, where ϕ is the angle between the magnetic moment and the magnetic field, the magnets being supposed distributed at random.

On the quantum theory the mean value of $\cos^2\phi$ for a discrete number of values of ϕ must be taken, so that a different value of $\overline{\cos^2\phi}$ is obtained for every different quantum number, where the bar denotes an average value. Pauli * has shown that :

$$\cos^2\phi = \frac{1}{3}\,\frac{(\mathbf{n} \qquad)(2\mathbf{n} + 1)}{2\mathbf{n}^2}$$

n being the number of Bohr magnetons in the elementary magnet. As **n** approaches infinity $\overline{\cos^2\phi}$ tends to 1/3, the value according to the classical theory.

Pauli excludes the case where the moment of the elementary magnet is perpendicular to the field. For $\mathbf{n} = 1$, $\phi = 0$, and all magnets are parallel to the applied field. For $\mathbf{n} = 2$, $\phi = 0$ or 60°, both directions being equally probable, and $\overline{\cos^2\phi} = \frac{5}{8}$. Thus, the number of Bohr magnetons in a given molecule is not an integral number, as it would be if all directions in space were permissible for the magnetic moments, but a fractional number, the value of which depends upon the number of space quanta allotted to the orbit. Taking the simplest case, **n** $= 1$, $\overline{\cos^2\phi} = 1$, so that $\sigma_0{}^2$ has the values :

---

* *Phys. Zeits.*, 21, 615 (1920).

$$\sigma_0{}^2 = 3RT\chi_M \quad . \quad . \quad . \quad \text{Langevin theory}$$

$$\sigma_0{}^2 = RT\chi_M \quad . \quad . \quad . \quad \text{Quantum theory}$$

Thus, according to the quantum theory, the value of the magneton is increased to $\sqrt{3}$ times the value of the Weiss magneton. As the value of the Bohr magneton is approximately five times that of the Weiss magneton, if **n** $= 1$, the value of the former should be $5\sqrt{3} = 8{\cdot}7$ times a Weiss magneton. Similarly, if **n** $= 2$ the value should be 13·7 times a Weiss magneton.

Experimental results show that the number of Weiss magnetons in O_2 and NO are 14·2 and 9·2, respectively, numbers which approximate closely to those calculated above for **n** $= 2$ and 1, respectively.

Paulis' theory has been modified by later workers, particularly Sommerfeld.* We have shown in Section 1 that the magnetic moment, resolved in the direction of the magnetic field, is mg Bohr magnetons, where m can take the values $+$ j, $+$ (j $-$ 1) . . . $-$ j. Under these conditions it can be shown that :

$$\chi_M = \frac{(\mathrm{j}gM_B)^2}{3RT} \cdot \frac{\mathrm{j}+1}{\mathrm{j}},$$

where M_B is the Bohr magneton per gram-atom.

If M_W is the value of the Weiss magneton, and p the number of Weiss magnetons per gram-atom,

$$\chi_M = \frac{1}{3}\frac{(pM_W)^2}{RT},$$

and from these two expressions,

$$p^2 = \left(\frac{\mathrm{j}gM_B}{M_W}\right)^2 \frac{\mathrm{j}+1}{\mathrm{j}},$$

or,

$$p = 4{\cdot}97\,\mathrm{j}g\sqrt{\frac{\mathrm{j}+1}{\mathrm{j}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

---

* *Zeits. f. Phys.*, **19**, 221 (1923) ; see also Hund, *ibid.*, **33**, 855 (1925).

since we know that $M_B/M_W = 4{\cdot}97$. Thus, the number of Weiss magnetons per gram-atom can be calculated for any atom or ion. The simplest case is that of atoms in an S state, when the magnetic moment is entirely due to the electron spins, *i.e.*, $g = 2$, $j = s$, so that :

$$p = 4{\cdot}97\sqrt{4s(s+1)} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Permitted values of s are 0, ½, 1, 1½, . . . corresponding to 0, 1, 2, 3 . . . unbalanced electrons, the magnetic moment being 0, 1, 2, 3, . . . Bohr units. For s = ½, 1, 1½, *etc.*, $p = 8{\cdot}6$, 14·1, 19·3, *etc.* Hund,* using expression (11) obtained values for p, which agreed closely with the experimental values for the rare earth ions. For the ions of the first transition group, however, the sequence of p values given by the theory was completely different from that observed.

Van Vleck,† in his treatment of paramagnetism on the basis of the new quantum mechanics, obtains the same expression (11) for the case where the multiplet intervals are large. When the multiplet intervals are small, he shows that the spin and orbital moments (s and l) are quantised separately, relatively to the axis of the field, and obtains in place of expression (11) :

$$p = 4{\cdot}97\sqrt{4s(s+1) + l(l+1)} \quad . \quad . \quad . \quad . \quad (12)$$

10. Susceptibility of Ions. Experimental measurements of the susceptibility of metallic ions are carried out, either with solutions, or with solid salts of the metals. If we suppose the susceptibility of a solution of a paramagnetic salt to be proportional to the concentration, we can attribute a certain susceptibility per unit mass to the dissolved salt. A correction must be made for the diamagnetism of the solvent. In many cases the susceptibility of the paramagnetic ion is large compared with that of the diamagnetic radical, combined with it in the salt. Now all atoms are essentially diamagnetic, the paramagnetism being superimposed, but a simple calculation shows that the subadjacent diamagnetism is negligible for the ions-scandium to nickel. Thus, we can obtain from the measurements made with solutions a value for the susceptibility per gram-ion χ_i of the metallic elements. In general, the solutions obey Curie's law, but as Fœx * has shown, very concentrated solutions may deviate from the law, and for such solutions the susceptibility, χ, follows the Curie-Weiss law, $\chi = C/(T - \theta)$. In either case the value of C may be determined experimentally, and both the saturation value $\sigma_0{}^2$ and the elementary magnetic moment, calculated.

---

* *Zeits. f. Phys.*, **19**, 221 (1923).
† *Phys. Rev.*, **31**, 587 (1928).

The apparent ionic susceptibility in many cases varies with the concentration. Thus with cobalt salts the value of p for Co^{++} varies between about 24 and 25; the addition of acid may cause the apparent p value to fall below 23. On the other hand, nickel chloride, in concentrations ranging from 0·62 to 22·69 per cent., gives a p value for Ni^{++} which is constant to within about 4 per cent., the value being practically the same for different salts. There are also indications that θ in the equation $\chi = C/(T - \theta)$ is not constant. Birch † has found with $CuCl_2$ in solution that from $0° - 40°$ C., $\theta = + 10$ and $p = 9{\cdot}01$; from 40°—85° C. $\theta = - 65$, $p = 9{\cdot}98$.

Most paramagnetic salts obey the Curie-Weiss law ‡ down to about 80° K., but some of them show deviations at lower temperatures, such that the susceptibility χ increases less rapidly with fall in temperature than is given by this law.

In addition, the value of θ depends on the content of water of crystallisation. Thus, for a series of nickel compounds, the θ's have the following values: $NiSO_4$, —79·4, $NiSO_4, 7H_2O$, + 62·2, $NiSO_4(NH_4)_2\,SO_4 . 6H_2O$, —4, and for the cobalt compounds: $CoSO_4.7H_2O$, — 13·7, $CoSO_4.(NH_4)_2SO_4.6H_2O$, —22. The values of θ in a series of similar substances do not follow necessarily the order of water of crystallisation of the substance, and may be positive, or negative, in the same series of compounds.

Jackson § showed that there is definite variation in the magnetic moment of different salts containing the same ion. In a series

---

* *Ann. d. Phys.*, **16**, 174 (1921).
† *Jour. d. Phys.*, **9**, 137 (1928).
‡ *Leiden Comm.*, Nos. 122 (a), 124 (a), 129 (b), 132 (e), 139 (c).
§ *Phil. Trans.*, *A*, **224**, 1 (1923).

of careful experiments he found the following values of p for different nickel salts :

$NiSO_4$ . . . . . $p = 16{\cdot}9$
$NiSO_4, 7H_2O$ . . . . $p = 14{\cdot}62$
$NiSO_4(NH_4)_2SO_4, 6H_2O$ . . $p = 15{\cdot}9$

The apparent p value, calculated by the standard method for the same ion in different salts, may vary considerably ; the same salt may also behave differently, magnetically, according to its thermal treatment, and give different p values over different ranges of temperature. The extensive investigation of Chantillon * on the cobaltous ion shows how widely the magnetic moment may vary (from 22 to 26).

The ions of the first transition series have been studied most completely ; this is the iron series, with from 18 to 28 electrons in the ions. Although there is considerable variability in the magneton values for some of the ions, for ions with the same numbers of electrons the values cluster closely round fairly well-defined means. These, however, do not correspond with those calculated by means of equation (10) from the anticipated ground states of the ions. It seems as if the orbital moment l and spin moment s are best considered separately. The ions behave as though they were free with respect to the spin moment, but not with respect to the orbital moment.

The magnetic moments of the ions of the first transition series,† calculated by means of equations (10), (11) and (12), are given in Table X. The experimental values have been included, the index giving the positive charge on the ion, and the calculated and observed results are also shown in Fig. 40. None of the suggestions so far made seem adequate to account even qualitatively for some of the distinctive magnetic characteristics of these ions of the first transition series. Stoner ‡ suggests that the p value should lie between :

$$4{\cdot}97\sqrt{4s(s+1)} \text{ and } 4{\cdot}97\sqrt{4s(s+1)+l(l+1)}.$$

---

* *Annales d. Phys.*, 9, 187 (1928).
† See Stoner, *Phil. Mag.*, 8, 250 (1929).
‡ *Ibid.*, 8, 250 (1929).

TABLE X. CALCULATED AND OBSERVED MAGNETIC MOMENTS OF IONS OF THE FIRST TRANSITION SERIES

Number of Electrons	19	20	21	22	23	24	25	26	27
$4{\cdot}97\sqrt{4s(s+1)}$	8·6	14·1	19·3	24·4	29·4	24·4	19·3	14·1	8·6
$4{\cdot}97g\sqrt{j(j+1)}$	7·7	8·1	3·9	0	29·4	33·6	33·2	28·0	17·7
$4{\cdot}97\sqrt{4s(s+1)+l(l+1)}$	14·9	22·2	25·8	27·2	29·4	27·2	25·8	22·2	14·9
Observed values of p									
Solutions			Cr^3 18·2–19·1	Cr^2 23·8	Fe^3 26–29·5 Mn^2 29·4	Fe^2 26·5	Co^2 23–25	Ni^2 16	Cu^2 9–10
Solid salts	V^4 8·9		Cr^3 18·9 M^4 19·8		Fe^3 29 Mn^2 27–30	Fe^2 25–27·5	Co^2 22–26	Ni^2 14·5–17	Cu^2 9–11

tending to the former value at low, and the latter at high, temperatures.

Very little is known about the magnetic properties of the second and third transition series, of which the most characteristic

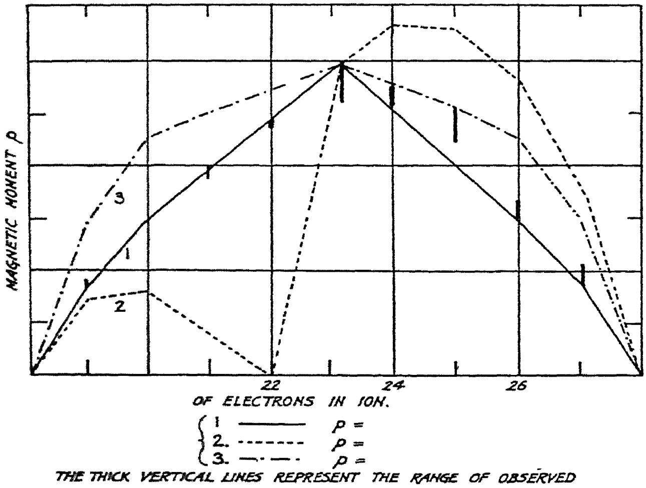


FIG. 40.—Calculated and observed magnetic moments of ions of the first transition series.

elements are Ru, Rh, Pd, Os, Ir and Pt. Cabrera and Dupérier * have examined the chlorides of these six metals and obtained the following results :

Ion.	Ru^{+++}	Rh^{+++}	Pd^{++}	Os^{++}	Ir^{+++}	Pt^{++}
$\chi \times 10^7$	+ 95·2	− 0·825	−2·09	+ 1·58	− 0·48	− 2·18
$\chi_A \times 10^7$	+1912·0	+45·5	+3·38	+82·75	+47·2	−17·4

Guthrie and Bourland † have also investigated the susceptibility of these metals. They found that Pd and Pt follow, approximately, a Curie-Weiss law, but that Ru, Rh, Os and Ir have paramagnetic susceptibilities which increase with temperature.

The rare earths have been investigated in detail by Cabrera and Dupérier,‡ who have shown that the sulphates and oxides of Gd, Tb, Dy, Ho and Er conform to the Curie-Weiss law, but that the specific susceptibilities of the sulphates and oxides of Nd, Sm and Eu are better expressed by the equation :

$$- \theta) = C.$$

The term k represents a susceptibility which is independent of temperature, and which is paramagnetic for elements in the neighbourhood of Sm, but diamagnetic for Tu and Yb. Its presence may be attributed to a deformation of the atom. The values found for p are as follows :

Ion.	Value of p.	Ion.	Value of p.	Ion.	Value of p.
La^{+++}	0	Eu^{+++}	17·92	Er^{+++}	46·98
Ce^{+++}	11·89	Gd^{+++}	40·07	Tu^{+++}	35·85
Pr^{+++}	17·89	Tb^{+++}	47·92	Yb^{+++}	21·64
Nd^{+++}	18·00	Dy^{+++}	52·25	Lu^{+++}	0
Sn^{+++}	7·64	Ho^{+++}	52·00		

It appears that the Gd ion exists in two magnetic states with 38 and 40 magnetons, respectively. The values of p provide very clear evidence for the division of the rare earths into two groupings. Hund has also derived satisfactory values for the

---

* *Comptes Rendus*, 185, 414 (1927).
† *Phys. Rev.*, 37, 303 (1931).
‡ *Comptes Rendus*, 188, 1640 (1929).

magnetic moments of the different ions from the basic terms of the corresponding spectra.

The behaviour of complex ions presents special difficulties. Weiss * suggested that the magnetic moment of a complex ion is equal to that of the normal ion of the same valence, or to that of a normal ion whose effective atomic number is greater by 4. One finds on applying this rule that the complex ferrous and cobaltic ions have no magnetic moment, the same as Cu^{+}, and that the complex ferric ions have the same moment as Cu^{++}. This is in accord with experiment. Weiss's suggestion is really a generalisation of Kossels' law † which states that if we consider, not the atomic number, but the number of extra-nuclear electrons actually present in the ion, we find that a given ionic susceptibility corresponds to a given number of electrons, no matter what the nuclear charge may be. Ions with the same number of electrons have the same susceptibility. Kossel's law has been verified experimentally by Cabrera.‡

Welo § has obtained several important results from an exhaustive study of the paramagnetism of 124 complex salts, all in the form of powders.

11. Low Temperature Results. The question whether paramagnetic substances would show a saturation-effect at high field-strengths, has always been considered a very important one. Although it can hardly be assumed that the susceptibility will remain independent of the field strength when the latter is very high, yet with the highest fields available this appears to be the case. Now, according to Langevin's theory, if we write $a = \mu H/kT$, as long as a remains below 0·75, the changes of susceptibility with the field strength escape the ordinary method of observation and, at ordinary temperatures, even a substance as strongly paramagnetic as oxygen gives for a, with a field of 100,000 gauss, a value which is less than 0·05. On the other hand, lowering the temperature does provide a means by which the observation of paramagnetic saturation might be attained, and liquid-helium temperatures have been used by Kamerlingh Onnes and his collaborators for this purpose.

---

* *Trans Amer. Electroc. Soc.*, **55**, 75 (1929).

† *Ann. d. Phys.*, 49, 229 (1916).

‡ *Journ. d. Phys.*, 3, 443 (1922).

§ *Phil. Mag.*, 6, 481 (1928).

They investigated gadolinium sulphate. In early experiments it was shown that this solid follows Curie's law down to the freezing-point temperature of hydrogen, and there was no sign of saturation which, as Langevin's theory indicates, if it existed at that temperature, would be ferromagnetic in its nature, since paramagnetic saturation at the corresponding value of a would not yet be clearly observable.

Later, Woltjer and Onnes * measured the magnetisation of the salt at the temperature of liquid helium, 1·31° K. Taking into account the difficulties of the experiment, the experimental and theoretical values of σ/σ_0 agree very well, and it may be concluded that powdered gadolinium sulphate, $Gd_2[SO_4]_3 . 8H_2O$, follows Langevin's formula down to 1·3° K.

The highest magnetisations obtained were about 84 per cent. of that corresponding to perfect parallelism of all the elementary magnets. For the Curie constant they found :

$$C = 0{\cdot}02024,$$

which indicates a value of $p = 38{\cdot}65$ Weiss-magnetons. This gives, for the field, 22,230 gauss, which they used,

$$a = 6{\cdot}982.$$

The saturation moment, calculated from the value of the susceptibility in comparatively small fields, is approximately equal to the saturation moment which would be observed in very strong fields.

Woltjer † investigated anhydrous $CrCl_3$, $CoCl_2$ and $NiCl_2$. With all of these salts, down to the temperature region of liquid-nitrogen, the susceptibility is independent of the field strength. At the lowest ethylene temperatures, all of them satisfy the relation $\chi(T - \theta) = C$, in which θ is found to be 32·5°, 20° and 67°, respectively. In the temperature region of liquid hydrogen, the susceptibility depends on the field strength, for $CrCl_3$ it decreases, but for $CoCl_2$ and $NiCl_2$ it increases with increasing field. With a

---

* *Comm. Phys. Lab. Leiden*, No. 167.

† *Ibid.*, No. 173.

given field strength, the susceptibility of $CrCl_3$ increases with falling temperature, that of $CoCl_2$ decreases a little, while for $NiCl_2$ the initial susceptibility slightly decreases.

Jackson * determined the susceptibility of the sulphates of iron, nickel and cobalt, both in the powdered and crystal form at the temperature of liquid hydrogen. While all these substances follow the Curie-Weiss law at relatively high temperatures, they show the following types of deviation at the lower temperatures.

(1) The susceptibility increases more rapidly with fall in temperature than is given by the law (cobalt ammonium sulphate, nickel ammonium sulphate).

(2) The curve of $1/\chi$ against T possesses a point of inflection (nickel sulphate heptahydrate).

(3) A maximum and a minimum value of the susceptibility occur in the region of the lowest temperatures (anhydrous nickel sulphate, anhydrous ferrous sulphate).

In the case of the crystals he measured the principal susceptibilities of cobalt ammonium sulphate and nickel heptahydrate over a range of temperatures from about 14° K. to 290° K. In both cases, each of the principal susceptibilities follows the Curie-Weiss law at the higher temperatures, but deviates therefrom at the lower temperatures. The Curie constant is the same for each of the three principal susceptibilities.

The curves of $1/\chi$ against T for ammonium sulphate consist of three parallel straight lines at the higher temperatures, but become concave towards the temperature axis at the lower temperatures; the magnitudes of the deviations from the straight-line law are in the inverse order of the values of the susceptibilities, as are also the values of θ in the Curie-Weiss law. Hence, each of the principal susceptibilities of this crystal increases more rapidly with fall of temperature than is given by the law, although it is followed at the higher temperatures.

In the case of nickel sulphate heptahydrate, each of the curves possesses a point of inflexion, the curvature changing from convex towards the temperature axis to concave, as the temperature falls below 70° K. Thus the principal susceptibilities show the

---

* *Phil. Trans.*, *A*, **224**, 1 (1923).

same type of dependence on temperature as does the mean susceptibility, though this is not generally the case.

12. Paramagnetic Gases. The great majority of gases, whose susceptibilities have been measured, are diamagnetic. According to theory, the electrons in a molecule which are paired with one another produce a diamagnetic effect, but an unpaired electron must give a magnetic moment to the molecule as a whole, and thus produce paramagnetism. The work of Soné [*] shows that of the various oxides of nitrogen, the two which have unpaired electrons, NO and NO_2, are strongly paramagnetic, while all the rest are diamagnetic. Besides these two gases, the only other substance with an odd number of electrons, which exists as a gas under ordinary conditions of temperature and pressure, is chlorine dioxide, ClO_2 (33 electrons). This gas is of an explosive nature, so Taylor and Lewis [†] used a solution of it in carbon tetrachloride. Even this dilute solution proved to be paramagnetic.

Oxygen, with sixteen electrons, is a striking exception to the association of diamagnetism with an even number of electrons. In the gaseous condition it follows Curie's law, $\chi T = C$. Bauer and Piccard [‡] have measured the susceptibility of this gas and of nitric oxide. The values obtained were :

Oxygen, $\chi \times 10^6 = 107{\cdot}8 \pm 0{\cdot}3$.
Nitric oxide, $\chi \times 10^6 = 48{\cdot}7 \pm 0{\cdot}25$.

The number of magnetons, calculated by the usual methods, are 14·2 and 9·2 for oxygen and nitric oxide, respectively. Wills and Hector [§] have obtained slightly different results for oxygen.

For liquid oxygen we have the relation

where θ is equal to 71 [||]. Perrier and Onnes [¶] also measured the susceptibility of mixtures of liquid oxygen and nitrogen. From their results they concluded that :

---

[*] *Sci. Rep. Tohoku Imp. Univ.*, 11, 139 (1922).

[†] *Proc. Nat. Acad. Sci.*, 11, 456 (1925).

[‡] *Journ. d. Phys.*, 1, 97 (1920).

[§] *Phys. Rev.*, 23, 209 (1924).

[||] See Onnes and Perrier, *Comm. Phys. Lab. Leiden*, No.

[¶] *Ibid.*. N

(1) The susceptibility of liquid oxygen becomes considerably greater in proportion as its concentration in the mixture diminishes, *i.e.*, the additive rule is by no means followed in mixtures of oxygen and nitrogen.

(2) The deviations from the Curie-Weiss law, shown by pure oxygen at low temperatures, are not an immediate consequence of the change of temperature, but are caused by the increase of the density, *i.e.*, by the distance between the molecules becoming smaller.

(3) The variation in density of the oxygen due to temperature changes only alters the specific magnetisation, without affecting the Curie constant.

Van Vleck has formulated a theory of the paramagnetism of gases by means of the newer quantum mechanics, using as a basis the Hund theory of molecular quantisation. Unlike previous theories it is not necessary to suppose the orbits are as freely oriented in molecules as in atoms. The calculated value of the susceptibility of NO agrees with the experimental value within 1·5 per cent. He also calculated the deviations from Curie's law. Recently Bitter[*] measured the susceptibility of NO at different pressures and at 296° K. and 216° K. De Haas and Capel[†] also measured the susceptibility of this gas from 292·1° K. to 112·77° K. Their results confirm Van Vleck's predicted value for the variation of the magnetic moment with temperature.

13. Ferromagnetism. To explain ferromagnetism Weiss introduced the idea of an internal or molecular magnetic field. As stated previously, he postulated that this molecular field was proportional to **I**, so that the total field H is given by :

$$H = H_A + \alpha\mathbf{I},$$

where H_A is the external field and α, a constant depending on the nature of the substance. Weiss supposed that the magnetic molecules are arranged in sets, or groups, *domains*, as we shall call them, which may be small crystals of which magnetic metals like iron are composed, and that these groups are usually magnetised

Proc. Nat. Acad. Sci., **15**, 638 (1929) ; see also Aharoni and Scherrer, . *f. Phys.*, **58**, 749 (1929).

K. Akad. Amsterdam, *Proc.*, **33**, 1

as strongly as possible, even in an apparently unmagnetised piece of the metal. Thus, an essential consequence of the molecular field hypothesis is that a substance containing magnetic carriers may be *spontaneously magnetised* below a certain critical temperature, if the molecular field is positive. Further, since an ordinary sample of a ferromagnetic is not necessarily spontaneously magnetised as a whole, the magnetisation in one direction must be assumed to extend only throughout the domains. An applied field has the effect of making this spontaneous magnetisation apparent as the directions of magnetisation in the domains tend to parallelism. By extrapolating to zero field, the magnetisation observed in high fields, the value of the spontaneous magnetisation appropriate to the temperature, *i.e.*, due to the molecular field alone, may be found. From the extrapolated value of the intensity of magnetisation at the temperature of absolute zero, when the carriers will be parallel to one another, the magnetic moment per atom can be determined.

Let us first consider the simple theory of ferromagnetism. As in Section (8) we have,

$$\frac{\sigma}{} = \coth\left\{\frac{\mu(H_A + \alpha\mathbf{I})}{kT}\right\} \qquad \frac{kT}{\qquad + \alpha\mathbf{I})}$$

and if H_A is zero,

$$\frac{\sigma}{\sigma_0} = \coth\frac{\mu\alpha\mathbf{I}}{kT} \qquad \frac{kT}{}$$

The latter equation gives σ as a function of the absolute temperature, T. To solve it let $\mu\alpha\mathbf{I}/kT = a$, so that :

$$a = \frac{}{RTM}$$

where ρ is the density and M, the molecular weight of the ferromagnetic. Consider the curves corresponding to the equations :

$$\frac{}{\sigma_0} = \coth a - \frac{}{a},$$

$$\frac{\sigma}{\sigma_0} = \frac{MRTa}{\alpha\rho{\sigma_0}^2}. \quad . \tag{13}$$

Let A (a') be the point of intersection of these curves (Fig. 41), so that the intensity of magnetisation **I** of a domain, when the external field is zero, is given by :

$$\mathbf{I} = \frac{kTa'}{\cdot}$$

and

$$\frac{MRTa'}{\alpha\rho\sigma_0},$$

where, as before, σ_0 is the saturation value of σ, *i.e.*, the value

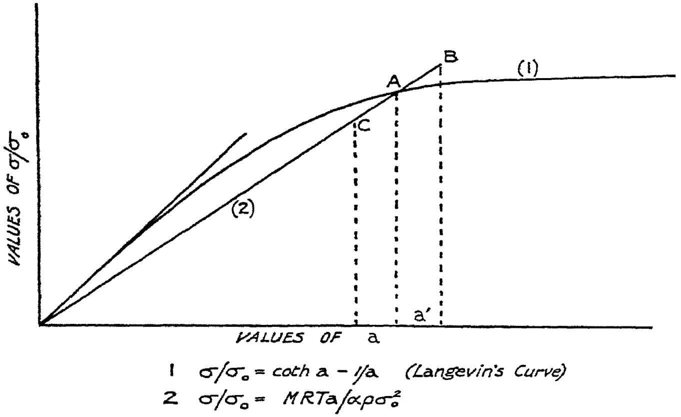


Fig. 41.—Spontaneous magnetisation of ferromagnetics.

of the magnetic moment per gram-molecule when H_A is very great.

As the temperature is raised, the slope of the line $\sigma/\sigma_0 = MRTa/\alpha\rho\sigma_0^2$ increases, so that the value of a' diminishes, until a temperature is reached at which a', and therefore σ, become zero. This is the *critical temperature* at which the ferromagnetic properties disappear. When $a' = 0$, the two curves touch each other at the origin, and $\frac{d}{da}\left(\frac{\sigma}{\sigma_0}\right.$; the same value for both curves.

Now for small values of a the equation :

$$\frac{\sigma}{\sigma_0} = \coth a - \frac{1}{a},$$

reduces to :

$$\frac{\sigma}{\sigma_0} = \frac{a}{3},$$

so that

$$\frac{d}{da}\left(\frac{\sigma}{\sigma_0}\right) = \frac{1}{3}.$$

Thus there will be a point of intersection of the two curves when the slope of the straight line is less than that of the tangent to the curves, *viz.*, 1/3,

i.e., when

$$\frac{MRT}{a\rho\sigma_0^2} < \frac{1}{3},$$

or

$$T < \frac{a\rho\sigma_0^2}{3MR} < \theta,$$

where θ is the limiting temperature at which spontaneous magnetisation just becomes possible. At higher temperatures the effect of molecular collisions is sufficient to overcome the tendency towards spontaneous alignment of the magnetic molecules. The state indicated by A (a') is stable under the spontaneous magnetisation. For if the molecules in a domain assume the state indicated by C, the local magnetisation is less than that corresponding to equilibrium. Hence the magnetisation, and so the field and the value of a increase until the state indicated by a' is reached. Similarly at B the local magnetisation is greater than the equilibrium value, as indicated by Langevin's curve, and the magnetisation and the field tend to decrease until the state a' is reached.

The spontaneous magnetisation cannot be identified with the quantity usually defined as remanent magnetism in describing the experimental hysteresis-loops. There is nothing in the theory to account for the initial hysteresis curve, *i.e.*, nothing to account for the gradual increase in **I** produced by applying a gradually increasing field to an initially demagnetised piece of iron. In fact, there is nothing to account for the existence of demagnetised pieces of iron at all. Every piece of ferromagnetic at a temperature below θ should possess, whenever it is not under the influence of an external field, the spontaneous magnetisation calculated from the intersection of the Langevin curve and the straight line of Fig. 41. This entails the idea of domains within the demagnetised

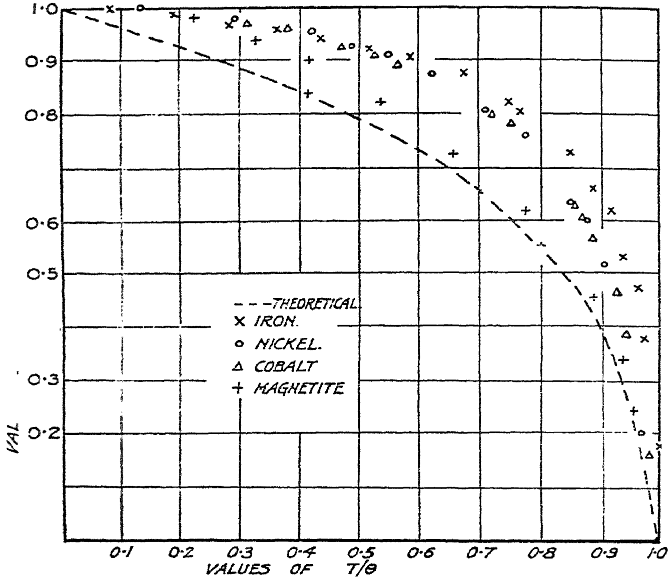


FIG. 42.—σ/σ_0 as a function of T/θ.

metal, each domain possessing the full spontaneous magnetisation of the theory, while in direction the magnetic moments of the domains are oriented entirely at random. It is not possible to identify these domains with individual crystals, nor with any other discernible granulations of the metal. As for the initial part of the hysteresis curve, attempts have been made to explain it, either by supposing that the increasing field orients the magnetic moments of the several domains gradually into parallelism with itself or, what is more probable, that the field abruptly reverses, one after the other, all of the magnetic moments which are inclined initially to it at angles greater than 90°.

Since θ, the Curie-point temperature, is equal to $\alpha\rho\sigma_0{}^2/3RM$, equation (13) may be written :

$$\frac{\sigma}{\sigma_0} = \frac{T}{\theta} \cdot \frac{a}{3},$$

or,

$$\frac{\sigma}{\sigma_0} = f\left(\frac{T}{\theta}\right),$$

such that at $T = 0, f\left(\frac{T}{\theta}\right) = 1$, and at $T = \theta, f\left(\frac{T}{\theta}\right) = 0$. Experimental data for iron, cobalt, nickel and magnetite below their respective Curie-points, together with the theoretical curve, $\frac{\sigma}{\sigma_0} - \frac{T}{\theta}$, are shown in Fig. 42. The agreement is good for magnetite, and fairly satisfactory in the cases of iron, nickel and cobalt, although the differences between the theoretical and the experimental results are greater than with magnetite. On the whole the theory gives a fairly satisfactory explanation of the variation of the saturation intensity of magnetisation of ferromagnetic substances with the temperature.

If the applied field is small, and the temperature high, we have :

$$\frac{\sigma}{\sigma_0} = \frac{a}{3} = \frac{\mu(H_A + \alpha \mathrm{I})}{3kT},$$

or

$$\frac{\sigma}{\sigma_0} = \frac{\sigma_0}{3RT}\left(\mathrm{H}_A + \frac{\alpha\rho\sigma}{M}\right),$$

so that

$$\chi_M = \frac{\sigma}{H} = \frac{\sigma_0{}^2}{3R(T - \theta)} = \frac{C_M}{T - \theta} \quad . \quad . \quad . \quad . \quad (14)$$

where

$$\theta = \frac{\alpha\rho\sigma_0{}^2}{3RM} = \frac{\alpha\rho}{M}C_M.$$

Hence ferromagnetics at high temperatures, *i.e.*, beyond the Curie-point, become paramagnetics. This may be illustrated by plotting $1/\chi$ as a function of the temperature. If this is done for nickel beyond the Curie-point, 360° C. approximately, the curve beyond 410° passes into a straight line which continues undeflected to 900° (Fig. 43). In the case of iron at temperatures beyond its Curie-point, 775° C., the points for temperatures between 920° C. and 1,395° C. lie along a straight line, which is sharply broken off at each end of that interval, being followed beyond 1,395° C. by what seems to be the commencement of an entirely different line, and preceded before 920° C. by a series of points which are well fitted by a pair of straight lines connected with each other at 828° C. The data for cobalt beyond its Curie-point, 1,130° C., likewise conform to a pair of connecting straight lines.

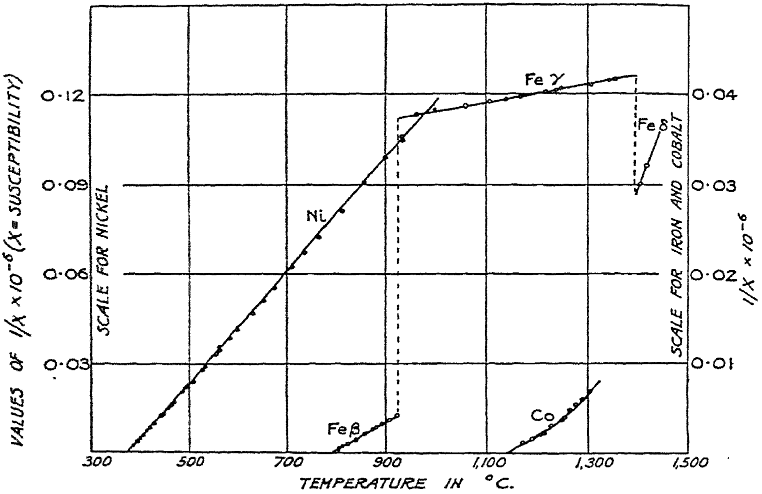


FIG. 43.—Susceptibility-temperature curves for iron, nickel and cobalt above their respective Curie-points.

According to this theory of ferromagnetism, the temperature at which the spontaneous magnetisation disappears—the Curie-point—should be equal to θ in equation (14) for the paramagnetism of the substance beyond the Curie-point. For nickel the agreement is good: 633° K. against 645° K., and there is also fair agreement for cobalt and iron.

14. Atomic Moments of Ferromagnetics. For each of the straight lines relating $1/\chi$ with T, the values of the constants C and θ may be computed, and from them the atomic magnetic moment and the coefficient α of the molecular field. In calculating the values of the moment μ of the elementary magnets it is assumed that there are as many elementary magnets per unit volume of metal as there are atoms. With this assumption the number of Weiss magnetons per gram-atom, p, are as follows:

Metal.	Temperature Range °C.	Values of θ.	Values of p.
Fe β_1 .	774–828	1047	20·9
β_2 .	828–920	1063	17·4
γ .	920–1395	−1340	28·2
δ .	1395–	1543	7·05
Co β_1 .	1170–1241	1404	15·9
β_2 .	1241–1303	1422	14·55
Ni . .	412–	645	8

All these values of p are approximately equal to those customarily found for paramagnetic gases and salts in solutions. The values of α are of the order of several thousands, so the postulated molecular field must therefore be supposed enormously greater than the applied field H_A. In one of these cases it must even be assumed antiparallel to the field H_A for θ is negative, and, consequently, so is α.

Since it is necessary to assign several distinct values to p in order to explain the behaviour of iron over various ranges of temperature, the iron atom does not possess a constant and characteristic magnetic moment, which is the source of ferromagnetism. These changes in p sometimes coincide with striking changes in the condition of the metal. Thus at 920° C. iron changes from a body-centred lattice of spacing 2·88Å, to a face-centred lattice of spacing 3·60Å. It retains the latter form as the temperature increases until 1,395° C., when it returns to the body-centred-cubic arrangement. These alterations in atom-lattice are attended by changes in the physical properties of the metal so great, that the modifications were distinguished long before atom-lattices were known. Changes in p sometimes occur apparently quite unaccompanied by changes in the atom-lattice, or other physical features. The variation occurring at 828° C. in iron is of this type, and so is the change in nickel which in occasional samples has values of p approximately equal to 9 instead of the usual 8 Weiss magnetons.

All these results refer to the paramagnetic susceptibility which ferromagnetics exhibit above the Curie temperature.

When the values of p are deduced from measurements on the saturation intensity at low temperatures, *i.e.*, ferromagnetic state, we find that there is no agreement between the two sets of p values.

As the magnetising field acting on a ferromagnetic specimen is gradually increased, we obtain the familiar $\mathbf{I} - H$ curve, and if the final part of the curve is extrapolated to zero field, we obtain the value of the spontaneous magnetisation at the temperature at which the experiment is performed. Thus, by carrying out experiments at very low temperatures, and extrapolating from the data to absolute zero, the value of $\mathbf{I}_s$ (saturated) may be determined. If the saturation signifies that all the atomic moments are parallel, then the magnetic moment of each must be the quotient of $\mathbf{I}_s$ by the number of atoms in unit volume.

Recently Weiss and Forrer * have deduced the atomic moments of iron, cobalt and nickel from saturation data relating to 25 ferro-cobalt alloys and 9 nickel-cobalt alloys at ordinary temperatures, and from their temperature coefficients down to the temperature of liquid air. They plotted the calculated number of Weiss magnetons p against the percentage composition of the alloy, and extrapolated the results to determine the value of p for the pure metal. Their results are shown in Fig. 44.

* *Proc. Phys. Soc.*, **45**, 413 (1930).

Weiss and Forrer found that like the *ions* of the iron group, the atoms of iron, nickel and cobalt are capable of assuming different atomic moments. The change of moment is not always associated with a change in the crystal lattice. Thus in alloys belonging to different ranges of atomic composition, α-iron has been found with moments of 11 and 15 magnetons, and γ-iron with a moment of 14 magnetons. Considering the Fe–Co curve *, there are two regions in which the moment varies in a strictly linear manner,

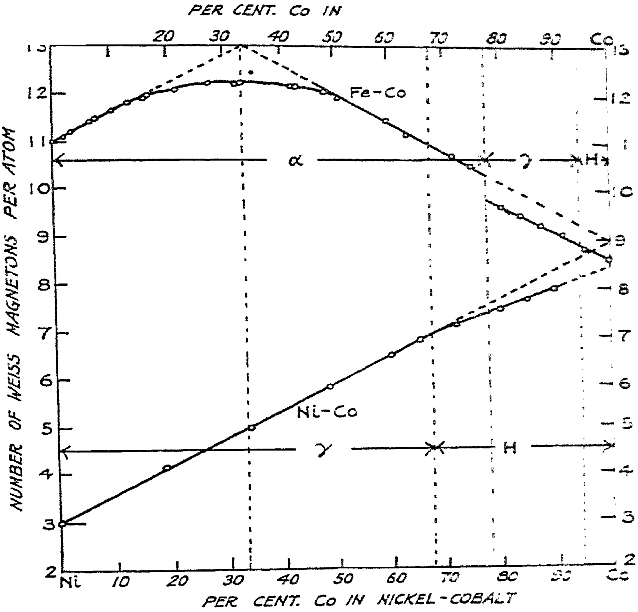


FIG. 44.—The atomic moments of ferromagnetics.

---

* At low temperatures, for alloys containing from 0 to 78 per cent. of Co, the stable structure is the centred cube (α-ferrocobalt), for those containing from 78 to 95 per cent. it is the face-centred cube (γ-ferrocobalt), and for those containing from 95 to 100 per cent. it is the hexagonal lattice of maximum density (H-ferrocobalt).

namely, those in which there is from 0 per cent. to 13 per cent., and from 50 to 78 per cent. of cobalt. The first straight line begins at the known iron-point of 11 magnetons, and if we assume that the other constituent, with fixed moment, is cobalt itself, and not a compound, we find by extrapolation a form of cobalt with 17 magnetons.

The second straight line reaches the axis corresponding to 100 per cent. of cobalt at the point where $p = 9$, so that cobalt, in α-ferrocobalts rich in that element, has, therefore, an atomic moment of 9 magnetons. If the straight line be produced as far as the iron ordinate, a form of iron with 15 magnetons is found.

In the γ region a further straight line may be observed which, when produced to the cobalt ordinate, gives us another moment for cobalt which is less than 9, and may be estimated to be 8·67 magnetons. If this straight line be produced backwards to the iron ordinate, a moment of 14 magnetons is obtained for γ-iron.

The nickel-cobalt curve * comprises two regions of linear variation. The first passes through the known point, $p = 3$, for nickel, and points towards the integer, $p = 9$, for cobalt. The second gives $p = 8{\cdot}5$ exactly, which agrees with the calculation from the measurements made by Kaya on a single crystal of cobalt in the direction of high susceptibility. When produced backwards as far as the nickel ordinate, this straight line gives a moment for nickel in the neighbourhood of 4.

Among the ten moments which the experimenters determined by means of these alloys, eight are integral multiples of the experimental magneton, 1125·6, and two are mixed numbers containing simple rational fractions, namely, $8\frac{2}{3}$ and $8\frac{1}{2}$. The atomic moments derived from saturation data at low temperatures are, therefore, like those derived by spectrum analysis, rational fractions of the natural unit furnished by the quantum theory.

15. Magnetisation of Single Crystals. Magnetic measurements are most directly interpretable when made on single crystals, but it is only fairly recently that ferromagnetic crystals, large enough to be studied, ceased to be a rarity. Only two kinds occur in nature: those of magnetite, a modification of one of the oxides of iron, Fe_3O_4, and those of pyrrhotite, a sulphide of iron, Fe_7S_8.

---

* Those nickel-cobalt alloys containing from 68 to 100 per cent. of cobalt are stable at low temperatures in a hexagonal crystal lattice of maximum density (H-nickel-cobalts), while the alloys containing less cobalt crystallise in a face-centred cubic lattice (γ-nickel-cobalts).

The well-known ferromagnetic substances, with two exceptions, crystallise in the cubic system. These exceptions are pyrrhotite and one modification of cobalt, both of which belong to the hexagonal system.

In cubic crystals, directions parallel to the edges of the cubes, to their diagonals, to the diagonals of their faces, are called the *tetragonal*, *trigonal*, *digonal* axes, or the *quaternary*, *ternary*, *binary* axes, respectively, the planes to which these directions are perpendicular being denoted by (100), (111), (110), respectively. Of the three lattices in which atoms may be arranged in a cubic crystal—*simple cubic*, *body centred*, *face centred*—iron conforms to the second, nickel and cobalt to the third. The iron-nickel alloys, containing more than 30 per cent. of nickel, follow the nickel lattice; the permalloys belong to this class, while those containing less than 30 per cent. of nickel are similar to iron.

Now when a magnetic field is applied to a crystal, it produces a magnetisation which is not parallel to the effective field, unless this field is parallel, either to a tetragonal, or to a trigonal, or to a digonal axis. If we apply a field parallel to the axis of a long rod, cut from a single crystal in such a way that this axis is parallel to one of the specified directions, the I-*H* curve rises much more sharply than does the normal curve for polycrystalline iron. The first segment of the curve is very short, and the second passes into the third while the field is still low. The slope of the first part of the curve, *i.e.*, the initial susceptibility, is greatest when the axis of the rod is a tetragonal axis of the crystal, less if it is a digonal axis, and least if it is a trigonal axis, though the differences are not great. This is expressed by saying that iron is most easily magnetised along the tetragonal axis, less so along the digonal and least along the trigonal. Experimental curves * for iron and nickel are given in Fig. 45. In the case of nickel the (111) axis is that of easiest magnetisation. The saturation value of the intensity of

---

* See Honda and Kaya, *Sci. Rep. Tohoku*, 15, 721 (1926); Kaya, *ibid.*, 17, 639 (1928).

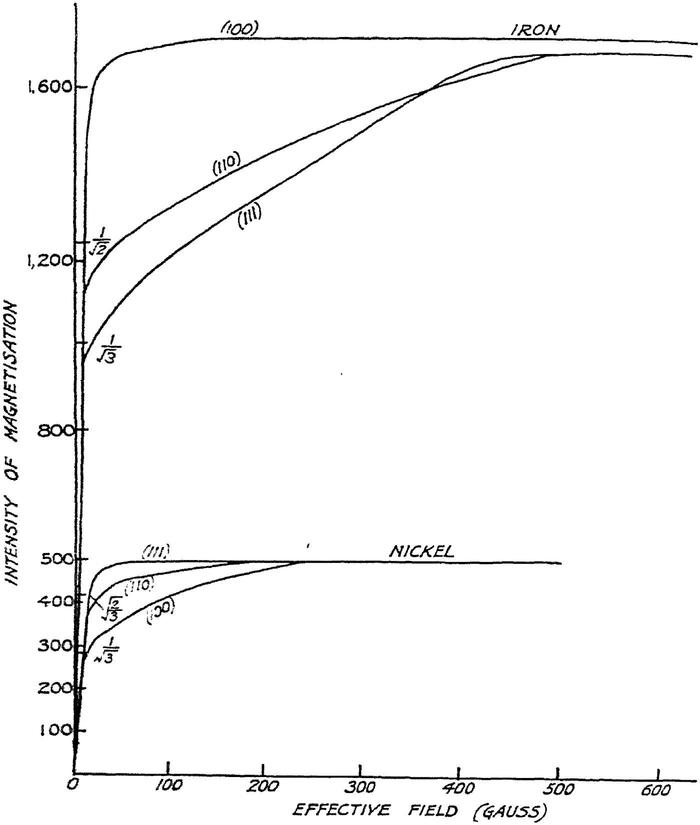


FIG. 45.—Magnetisation curves for iron and nickel single crystals.

magnetisation, when it is finally attained, seems always to be about the same.

In an unmagnetised iron crystal, each of the domains will be fully magnetised, but so oriented at random along (100) directions that there is no resultant magnetic moment. Now there are two fundamentally different ways in which bulk magnetisation occurs in the crystal. The first is a change from one cubic axis to another, and takes place in fields * of a few gauss; the second is the departure from a cubic direction, and occurs only in comparatively large fields. These may be associated, respectively, with the initial rapid rise up to, and the slow increase after, the steep part of the ordinary **I**-H curve. The value of the intensity of magnetisation, at which the break occurs, will depend on the direction of the magnetic field, relative to the crystal axes. When all the small elements in the crystal of iron have had their direction of magnetisation changed, to coincide as far as possible with the cubic directions nearest to the applied field, consistently with the condition that there shall be no transverse magnetisation, then any further increase of bulk magnetisation must be produced by forced deviations from these cubic axes, towards the direction of the applied field, and the so-called knee in the **I**-H curve will appear.

With an applied field along a cubic axis, the second process will not appear at all, and the initial rapid rise should continue right up to complete saturation. For the (110) and (111) directions the transition should take place at intensities $1/\sqrt{2}$ and $1/\sqrt{3}$ of the saturation values. In the case of nickel, where the (111) axis is that of easiest magnetisation, this will be the direction for which there is no break in the **I**–H curve; while for the (110) and (100) axes the breaks will occur at $\sqrt{2/3}$ and $1/\sqrt{3}$ of the saturation values. The experimental results are shown in Fig. 45, but in view of the difficulty of obtaining perfect single crystals of these metals, sharply-defined breaks cannot be expected. The actual agreement between theory and experiment is good.

16. Magneto-thermal Phenomena. On the basis of his theory of the internal molecular field Weiss † predicted a discontinuity in the specific heat of a ferromagnetic substance in the region of its Curie point. The mutual potential energy E of a number of elementary magnets, each of moment μ, and making an angle ϕ with the applied field H, is given by:

---

* See Honda, Masumoto and Kaya, *ibid.*, 17, 118 (1928).

† *Journ. d. Phys.*, 7, 249 (1908). The large change of specific heat on passing through the Curie point is the essence of the phenomenon of recalescence.

$$E = -\tfrac{1}{2}\sum \mu H \cos\phi,$$

so that when we consider a cubic centimetre of the given substance, we may write:

$$E = -\tfrac{1}{2} H\mathbf{I},$$

where $\mathbf{I}$ is the intensity of magnetisation. In the case of a ferromagnetic substance there exists the Weiss molecular field, $\alpha\mathbf{I}$, so that if we consider the intrinsic or spontaneous magnetism,

$$E = -\tfrac{1}{2}\alpha\mathbf{I}_0^2,$$

where $\mathbf{I}_0$ is the intensity of spontaneous magnetisation per c.c. Since E is negative, we must provide heat in order to demagnetise the substance, and the amount of heat necessary to demagnetise 1 gram of the substance is, therefore,

$$\frac{\alpha}{\rho}\mathbf{I}_0^2,$$

where ρ is the density of the substance and J, the mechanical equivalent of heat. Now $\mathbf{I}_0$ varies with temperature, so that the heat necessary to demagnetise a substance results in an apparent increase of its specific heat by an amount:

$$\frac{\partial}{\partial T}\left(\frac{1}{2J}\cdot\frac{\alpha}{\rho}\mathbf{I}_0^2\right) = \frac{1}{2J}\frac{\alpha}{\rho}\frac{\partial}{\partial T}\mathbf{I}_0^2.$$

From curves showing the variation of magnetisation with temperature, Weiss concluded that the specific heat of a ferromagnetic substance should rise to a maximum at the critical temperature, and then decrease continuously owing to the sudden disappearance of the magnetic term at that temperature.

Sucksmith and Potter [*] have pointed out that in the experiments confirming this, the magnetic and calorimetric data for the same substance should be measured simultaneously, and they carried out experiments on specimens of nickel and Heusler alloy, in which the specific heat was measured at different temperatures by a modification of the Nernst-Eucken method, the magnetisation being simultaneously measured by a ballistic method. Measurements were thus made up to 410° C. Their results are markedly different from what would be expected on the Weiss theory. They found in the case of pure nickel, for example, that the specific heat rose to a maximum as Weiss predicted, but the increased specific heat extended over a range of some 26° C. above the critical temperature.

---

[*] *Proc. Roy. Soc., A*, **112**, 157 (1926).

Bates,[*] using manganese arsenide, which possesses a convenient and sharply defined magnetic critical temperature in the neighbourhood of 45° C., found that the specific heat rose to a sharp maximum at 42·2° C., and then decreased rapidly. The form of the specific heat curve was similar to that which would be expected on the Weiss theory. The sharpness with which the magnetic critical point was defined, indicated that the curves $\partial \mathbf{I}_0$ and $\partial \mathbf{I}_0^2/\partial T$ were somewhat similar in shape to the specific heat curve, but whereas the first curve exhibited a maximum at 42·2° C., the second exhibited a maximum at 41·5° C.

When a ferromagnetic substance is suddenly inserted into a magnetic field, thermodynamical reasoning[†] shows that, if the process is reversible, an adiabatic rise in temperature, $\varDelta T$, results according to the equation :

where $\varDelta H$ is the increase in field strength and s_H, the specific heat of the substance when the field is constant. For a positive increment of H, $\varDelta T$ is positive, since $\partial \mathbf{I}_0/\partial T$ is negative. A similar adiabatic fall in temperature should occur when the field is decreased suddenly. Calculations show that if manganese arsenide were suddenly placed in a magnetic field, its temperature would be raised, and its magnetic properties more or less permanently changed, due to the fact that on losing its magnetism at 45° C., it does not become ferromagnetic again until it has been cooled to below 34° C., and if it is heated, say, to 43° C. and then cooled, its magnetic properties remain practically constant over

[*] *Ibid.*, 117, 680 (1927).

[†] See Weiss et Fœx, "Le Magnétisme," p. 148 (1926).

several degrees. In other words, its magnetic properties, after it has been placed in, and withdrawn from, a magnetic field, should correspond to those at a temperature higher than that which it initially possessed.

The presence of this effect provides a possible explanation for most of the lack of agreement between experimental results and the Weiss theory: Bates[*] accordingly carried out experiments to measure the variation of $\mathbf{I}_0^2$ with temperature in the absence of such disturbances. In Fig. 46 are plotted the values of the specific heat (continuous curve) and $\partial \mathbf{I}_0^2/\partial T$ (broken curve). It is

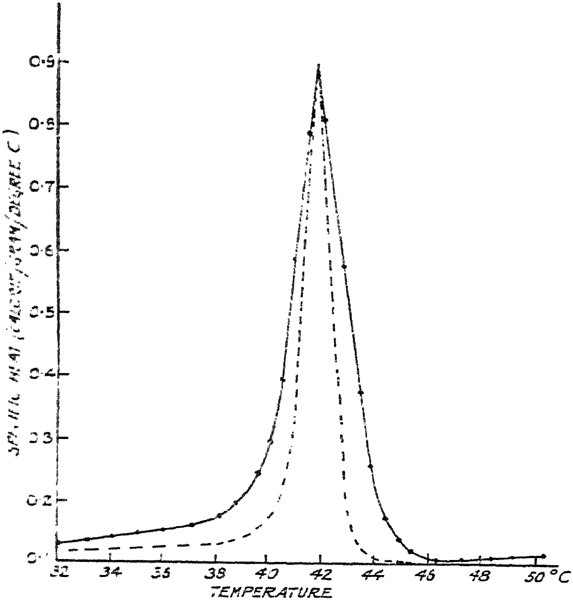


Fig. 46.—Variation of specific heat (full line) and of $\partial \mathbf{I}_0^2/\partial T$ (broken line) with temperature.

---

[*] *Proc. Phys. Soc.*, **42**, 441 (1930).

quite clear that the specific heat maximum and that of $\partial \mathbf{I}_0{}^2/\partial T$ occur at the same temperature, but the specific heat curve differs in several particulars from that for $\partial \mathbf{I}_0{}^2/\partial T$. Measurable specific heat changes occur before $\partial \mathbf{I}_0{}^2/\partial T$ has appreciably changed, and even if the marked changes in the specific heat end concurrently with the disappearance of $\partial \mathbf{I}_0{}^2/\partial T$, there is no doubt that the specific heat is considerably greater just before the magnetisation disappears than the Weiss theory would lead us to expect.

We may calculate the maximum value which the specific heat should possess on the Weiss theory. The value of α from susceptibility experiments * may be taken to be 3390, ρ, 6·02 gram per cubic centimetre, and $\frac{1}{2}\partial \mathbf{I}_0{}^2/\partial T$ at 42·2° C. to be 1560 c.g.s. units per gram, so that the additional specific heat at 42·2° C. is found to be 0·67 calorie per gram per degree. Hence the total specific heat at this temperature should be 0·77 whereas the maximum measured specific heat was 0·8.

Fowler and Kapitza † have developed the treatment of the specific heats of ferromagnetic substances along the lines of Heisenberg's theory of ferromagnetism, and predict a step-down in the specific heat, at the magnetic critical point of a ferro-magnetic substance, of approximately 3 calories per gram-molecule per degree. The step-down given by the Weiss theory, and by experiment in the case of magnanese arsenide, is of the order of 100 calories per gram-molecule per degree.

Now Fowler and Kapitza's expression for the specific heat contains two factors; one is $\partial \xi^2/\partial T$, where ξ is the ratio of the magnetisation $\mathbf{I}_0$ to the saturation value $\mathbf{I}_s$, acquired at very low temperatures, or high magnetic fields. At the magnetic critical point θ this factor may be taken as equal to $3/\theta$, which agrees with the experimental data for manganese arsenide. The discrepancy between the experimental and theoretical results must therefore be attributed to the remaining factor, which depends on the interaction integrals of two similar interacting systems, each containing one magnetisable electron. Bates concludes that the magnetism of the arsenide is due to interacting systems, each

---

* See Bates, ***Phil. Mag.***, **8**, 714 (1929).

† ***Proc. Roy. Soc.***, ***A***, **124**, 1 (1929).

containing more than one magnetisable electron. Fowler and Kapitza suggest that a theory to take account of more than one such electron will differ from that already developed by them only in complication of detail, and will give a value for the step-down of two or three times that mentioned above. In the case of the arsenide the step-down is at least thirty times the value predicted by the theory.

The numerical values obtained by Sucksmith and Potter vary from about 0·9 to about 1·34 calories per gram-molecule per degree, depending on the specimen of nickel. Thus their result is in approximate agreement with Fowler and Kapitza's prediction, but their theory is no more successful than the Weiss theory in explaining why the step-down in the case of nickel extends over such a wide temperature range, or why the specific heat continues when the magnetism has disappeared. For nickel, Weiss gives 1·67 calories per gram-molecule per degree for the step-down, whilst Klinkhardt * gives 1·47. Fowler and Kapitza remark that they would expect the step-down to be rather less than three, o the above numbers may be taken to indicate that the magnetic ehaviour of nickel is due to the interaction of systems, each ning one magnetisable electron. For iron, Weiss, Piccard and Carrad † give 6·8 calories per gram-molecule per degree for the step-down.

Another feature which requires explanation is the large minimum value of the specific heat above the magnetic critical point. In the case of iron and nickel we always find minimum values which give atomic heats much greater than the limiting values for other metals. This is particularly emphasised by Klinkhardt's measurements on the specific heat of iron. His minimum value for the specific heat of Feβ is about 10·3 and for Feγ, 8·6 calories per gram-atom per degree C.

Dorfman, Jaanus and Kikoin ‡ suggested that the step-down in the specific heat at the Curie point may be due partly to the positive ions and partly to the free electrons. If we write Δs_A for

---

* *Ann. d. Phys.*, **84**, 167 (1927).
† *Arch. Sci. Phys. Nat.*, **43**, 22, 113, 199 (1917).
‡ *Zeits. f. Phys.*, **54**, 277 (1929).

the step-down in the specific heat per atom, Δs_i, due to the positive ions and Δs_e, to the free electrons :

$$\Delta s_A = \Delta s_i + n\Delta s_e.$$

where n is the number of free electrons per atom. If only the free electrons are involved in the ferromagnetism of the metal, $\Delta s_i = 0$. if only the positive ions, $\Delta s_e = 0$. Now Δs_A is measurable directly calorimetrically, and Δs_e is obtainable from the sharp change in the *Thomson coefficient* $T\frac{\partial^2 \mathbf{E}}{\partial T^2}$ at the Curie point. They measured $T\frac{\partial^2 \mathbf{E}}{\partial T^2}$ in the neighbourhood of the Curie point (630° *K*) for nickel, and deduced the value $4{\cdot}8 \times 10^{-24}$ calorie per degree for Δs_e, whereas the experimental value for Δs_A is $3{\cdot}87 \times 10^{-24}$ calorie per degree. The fact that Δs_A and Δs_e are of the same order of magnitude is explained by supposing that the free electrons are alone concerned in ferromagnetism. Further, since these do not move in closed orbits, the magnetic moment they produce must be due to their intrinsic spin. It is shown that $\Delta s_e = 4{\cdot}8 \times 10^{-24}$ calorie per degree, leads to a value of the spin moment of the conduction electron equal to one Bohr magneton. The number of free electrons in nickel at the Curie point is shown to equal only 78 per cent. of the number of atoms ; at the absolute zero it is estimated that the number is reduced to 60 per cent.

Gerlach * has found that if a piece of nickel wire is kept at a temperature T_1 of about 20° C., and the temperature T_2 of the other end is raised, then a magnetic field parallel to the temperature gradient creates an electromotive force which steadily increases, and reaches an approximately constant value as soon as T_2 exceeds the Curie point. If T_1 be now increased, while T_2 is kept at any given temperature above the Curie point, the electromotive force, created by the magnetic field, decreases, and becomes zero as soon as T_1 is equal to the temperature of the Curie point. The electromotive force remains constant as long as the field effect is constant. It is independent of the course of the temperature fall and depends only on the temperature difference.

* *Proc. Phys. Soc.*, **42**, 418 (1930) ; *Ann. d. Phys.*, **8**, 649 (1931).

This effect is connected in the same way with the magnetisation as is the change of resistance at constant temperature. It is also connected with the reversible part of the ferromagnetic magnetisation.

17. Magneto-mechanical Effects. One of the most important magneto-mechanical effects is that of magnetostriction, the phenomenon of the change in dimensions which occurs when the magnetisation of a body is altered. On the whole this effect had not, until comparatively recently, thrown much light on the nature of the magnetisation, due to the fact that in most experiments the specimens consisted of an aggregate of micro-crystals, having an ill-defined and varying structure. More information is likely to be afforded by experiments made with single crystals, such as those performed by Honda and Kaya* with nickel, and by Webster† with iron. The variation of length with intensity of magnetisation is shown in Fig. 47 for the three simple directions in iron and nickel. In the direction of easiest magnetisation in each metal there is a gradual change of length, in one case an expansion, and in the other a contraction, beginning with quite small intensities, and gradually increasing as saturation is

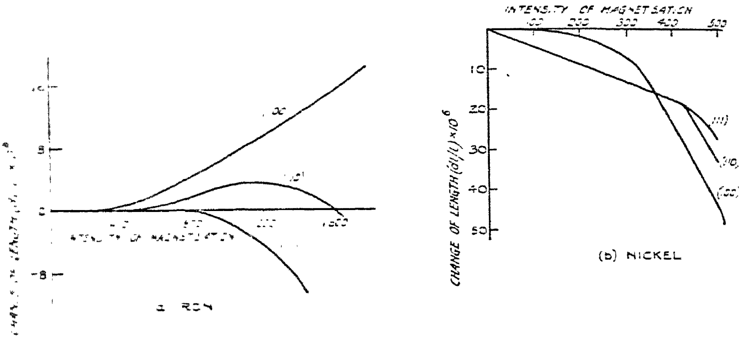


Fig. 47.—Magnetostriction curves for iron and nickel single crystals.

---

* *Sci. Rep. Tohoku*, **15**, 721 (1926).

† *Proc. Roy. Soc.*, A, **113**, 196 (1926).

approached. In the direction farthest removed from the above there is no appreciable change of length until approximately half-saturation, when a contraction sets in and rapidly increases with the magnetisation.

Akulov * explains magnetostriction as due to the distortion of the crystal lattice accompanying the rotation of the direction of magnetisation away from the direction of easiest magnetisation. His theory accounts for the difference in length of unit rods parallel to the different crystal directions when completely magnetised, but it does not account, for example, for the increase in length occurring when a rod of iron, parallel to a cubic axis, is magnetised. He shows, however, that a cube of iron, supposed completely devoid of magnetisation, on an atomic scale becomes slightly distorted when it acquires its normal spontaneous magnetisation. It becomes longer along the cubic axis of magnetisation than along those axes at right angles. The magnitude was not calculated, but it must be at least of the same order as the deviational distortion. Demagnetised iron must therefore be considered as a mosaic, made up of small asymmetrical volumes with their direction of distortion distributed equally along the three cubic axes. The resultant dimensions of a cube of demagnetised iron will be symmetrical, but will be a complicated average between the two dimensions of the distorted magnetised cube. When magnetisation takes place along a cubic axis, there must be a longitudinal expansion, with a lateral contraction, gradually increasing as the various small volumes become parallel.

For the (110) direction, as magnetisation proceeds, there is at first a concentration of the axes of distortion of many small volumes along the two cubic axes nearest the direction of magnetisation. There must be, therefore, an initial expansion which continues till the third axis has been completely abandoned. Further increase of magnetic intensity can only be produced by deviation from the cubic axes, and the corresponding contraction is sufficiently large to overwhelm the expansion due to increasing uniformity.

---

* *Zeits. f. Phys.*, 52, 389 (1928) ; 54, 582 (1929)

For the (111) axis, the three cubic directions are symmetrically disposed, and there is no real increase in uniformity before the deviational distortion appears ; consequently no initial expansion is observed.

McKeehan * has also formulated a theory of magnetostriction which depends upon interatomic forces.

The study of magnetostriction has recently become important because it promises to throw light on the obscure aspect of interatomic forces in solids. While only a few solids are ferromagnetic it is encouraging to observe that, as solids, they are not abnormal. If, then, the interplay of atoms in these solids can be followed by magnetic means, it is probable that any conclusions arrived at will apply equally well to solids, not themselves amenable to magnetic control, or measurement.

When the temperature of a ferromagnetic crystal passes through the Curie point, the crystal shows an anomalous expansion, or contraction. This change of length is greater than the ordinary magnetostriction effect, but of the same order of magnitude. The variation of the latter change in different directions in a single crystal of iron is as great as 35×10^{-6} per unit length. For the anomalous change of length the following values have been obtained below the Curie point :†

Iron. Curie Point. 768° C.

$$\frac{\delta l}{l} = +1{\cdot}1 \times 10^{-4}.$$

Nickel. Curie Point. 374° C.

$$\frac{\delta l}{l} = -0{\cdot}9 \times 10^{-4},$$

where δl is the change in length of a length l of the substance.

These changes in size are too great to be explained by purely magnetic forces. Heisenberg's theory of ferromagnetism supposes that magnetisation is accompanied by a change in the strength of binding between atoms, and the calculated resulting changes in the

---

* *Reviews of Modern Physics*, **2**, 477 (1930). See also Perrier, *Helv. Phys.* ., **4**, 213 (1931).

† See Powell, *Proc. Phys. Soc.*, **42**, 390 (1930).

size of crystals of iron and nickel at their Curie points are of the same order of magnitude as those observed.

The change of size which accompanies magnetisation varies continuously from the Curie point to saturation, but does not affect measurements of magnetostriction at ordinary temperatures.

18. The Barkhausen Effect. When a ferromagnetic substance is magnetised by a field which changes continuously, it is found that a part, at least, of the resulting change in intensity of magnetisation takes place in sudden discontinuous jumps. This is the *Barkhausen effect*, and may be investigated in the following manner.

Imagine a ferromagnetic substance encircled by a magnetising coil through which the current is being steadily increased, encircled also by a loop of wire which is connected to any instrument which continuously records the electromotive force, induced in the loop by the changing magnetisation. Since the magnetising field is being increased continuously, we should also expect the induced electromotive force to vary continuously, if the magnetisation increases in a continuous manner. It is found, however, that the induced electromotive force changes by small, but sudden jumps, and if the loop is connected to a telephone-receiver, through an amplifier, one hears a rustling, or crackling sound.

If the loop is connected to an oscillograph, and the magnetising field increased very slowly, the actual number of peaks in the oscillograph curve may be counted. It has been estimated that the process of magnetising a cubic centimetre of iron involves several thousand of these jumps. By measuring the area included within each of the peaks in the oscillograph curve it is possible to calculate the magnetic moment of a magnet, the creation of which has resulted in such a peak. In this way Tyndall * estimated that one such magnetic moment was 0·0027, which is much too large to identify the magnet with an individual atom, since a magnetic moment of 0·0027 is approximately equal to that possessed by a piece of saturated iron of 0·12 mm. edge. Neither can the magnet be identified with individual crystals, since a single crystal of a ferromagnetic makes as much noise in the telephone-receiver, while magnetised, as a fine-grained sample.* Thus, the data support the idea of magnetic domains, which are larger than atoms and smaller than crystals. Another interesting fact is that the Barkhausen effect is associated with the steep part of the ordinary magnetisation curve, which corresponds to the occurrence of irreversible changes of direction of magnetisation throughout domains. The initial and final nearly horizontal parts of the curve show no effect. Bozorth † estimated that the Barkhausen discontinuities account for most, if not all, of the whole change in magnetisation where the curves are steep. It is not yet decided whether the 10^{15}, or so, atoms which co-operate in a discontinuity of average size are all the atoms in a sharply-bounded region, or whether they form chains or networks, with unaffected atoms lying between them. The smallness of the effect of grain-size upon ferromagnetic properties, and the fact that the Barkhausen phenomenon of ordinary magnitude occurs in large single crystals, show that the grain, or crystallite, as we ordinarily understand it, is not magnetically homogeneous. Only when a substance is finely divided, or made into a very thin film,‡ do its intrinsic magnetic properties undergo any important changes.

---

* *Phys. Rev.*, **24**, 439 (1924).

Heaps and his collaborators § investigated the effects in minute specimens, where the discontinuities may be few and relatively large. The most recent results show that large discontinuities in magnetisation are accompanied by discontinuous changes in length, *i.e.*, by magnetostrictive jumps. Such changes in length had previously been observed by Arkadiew,‖ who simply listened to a telephone-receiver diaphragm, actuated by the tightly-stretched specimen as it was subjected to a magnetic cycle, but the simultaneity of length and magnetisation changes was not then demonstrated. Studies by Preisach ¶ show that the jumps in the magnetisation may be made enormous (or run together so as to be difficult of separate observation) by tension or torsion, and

---

* See Auwers and Sizoo, *Zeits. f. Phys.*, **60**, 576 (1930).

† *Phys. Rev.*, **34**, 772 (1929); **35**, 733 (1930).

‡ See Welo and Baudisch, *Phil. Mag.*, **3**, 396 (1927); Howey, *Phys. Rev.*, **34**, 1440 (1929).

§ *Ibid.*, **34**, 937 (1929); **36**, 326 (1930).

‖ *Comptes Rendus*, **184**, 1233 (1927).

¶ *Ann. d. Phys.*, **3**, 737 (1929).

Sixtus and Tonks * report a kind of trigger action, by which a local increase in the applied magnetising force can set-off a discontinuity, which progresses far beyond the region in which it started. The relatively slow propagation of such waves of magnetisation—much slower than the velocity of sound in the medium—may be wholly accounted for by eddy currents. It is attractive to speculate, however, that the delay may be due, in part, to the necessity for waiting before each advance for a favourable condition as regards energy of thermal agitation, and that we may yet trace a continuous progression of phenomena, from the almost instantaneous response of the atomic magnet to the slow secular variation of magnetic moment in well-aged magnetic steel.

The coalescence of microscopic Barkhausen discontinuities into major effects was first observed by Forrer † in suitably overstrained nickel wires. The abnormal values of remanent magnetism which he observed led him to postulate a rather complicated unitary magnet in this metal, the two parts of which might take up either of two configurations in the absence of an applied field. The high value of the remanent magnetism corresponded to a preponderance of the usually less numerous configuration. He extended the same reasoning to iron, in which he supposes that the unit must have three parts, and in a recent paper ‡ he suggests that the different types of hysteresis loop in iron form experimental evidence in favour of his hypothesis.

There appears to be a very close relationship between the magnetostriction effect and the Barkhausen effect. One phenomenon has not so far been observed in a substance without the other, and both are affected by heat treatment and mechanical strain. Now the two effects of tension, say on a nickel wire, are to produce a decrease in magnetic permeability, and a relatively larger increase in the magnetostrictive contraction, for a given intensity of magnetisation. Consequently, when the specimen is magnetised, a volume element will contract more than the surrounding material, in spite of its abnormally low intensity of

---

* *Phys. Rev.*, **35**, 1441 (1930); **37**, 930 (1931).

† *Journ. d. Phys.*, **7**, 109 (1926); **10**, 247 (1929).

‡ *Comptes Rendus*, **190**, 1391 (1930).

magnetisation, and the initial tension will increase until eventually there is some sort of slipping, or rearrangement of the material, and the tension is partially, or completely, released. This release causes a measurable change in length of the specimen only when the cross-sectional area of the volume element is an appreciable part of that of the whole specimen. The sudden length change should thus be more prominent in fine wires. The release of tension also causes a sudden increase in the permeability and intensity of magnetisation of the volume. Thus arises the Barkhausen effect.

19. The Gyromagnetic Effect. If we account for the general properties of magnetic substances by assuming as elementary magnets, electrons circulating in closed orbits, the planes of which in the case of para- and ferromagnetism are orientated by the magnetic field, it is evident that the process of magnetising, say, a suspended iron wire, involves a type of recoil, *i.e.*, the suspension of the wire should receive an opposite angular momentum and so experience a torque. This phenomenon and its converse are jointly called the *gyromagnetic effect.*

If μ is the magnetic moment and p the mechanical moment of an orbital electron, it may be shown[*] that,

$$\mu/\mathrm{p} = \mathbf{e}/2m_0c,$$

where $\mathbf{e}$ is the electronic charge, m_0, its mass and c, the velocity of light. Experimental results[†] give a value of μ/p, which is twice as great as that obtained by inserting numerical values in the above equation.

Now, according to spectroscopic evidence,

where g is the Landé splitting factor, so that the measurement of the gyromagnetic ratio enables one to calculate the mean value of g. For all the ferromagnetic substances investigated, $g = 2$ within the limits of experimental error. This, interpreted on modern theory, indicates that ferromagnetism is due to the spin of the electron. It does not necessarily mean that the carriers are free electrons. They may be free, or they may be electrons in atoms free to change their direction of spin.

---

[*] See Section 1.

[†] See Einstein and Haas, *Verh. d. deut. Phys. Gesell.*, 17, 152 (1915); Chattock and Bates, *Phil. Trans.*, *A*, 223, 257 (1922); Sucksmith and Bates, *Proc. Roy. Soc.*, *A*, 104, 499 (1923)

For paramagnetic materials theory and experiment indicate that the magnetic moment is due, in general, to the resultant of orbital and spin moments. Until recently, however, the gyromagnetic effect for paramagnetics had not been measured, since they could not be strongly enough magnetised. Sucksmith * has now devised a method for measuring the ratio μ/p and results have been obtained for the Dy^{+++} ion in Dy_2O_3. The value of g is calculated by means of the two formulæ,†

$$p = 14{\cdot}07\, C_M^{\frac{1}{2}}.$$

and

$$p = 4{\cdot}97g\sqrt{j(j+1)}.$$

For Dy^{+++} $j = 15/2$, and the number of Weiss magnetons, p, calculated from these two formulæ is 53, whereas susceptibility determinations gave 52. The measurements of the gyromagnetic ratio for this ion give the value of g as $1{\cdot}28 \pm 7$ per cent., in excellent agreement with the theoretical value 4/3.

Preliminary measurements on the gyromagnetic ratio have also been made by Sucksmith ‡ on Mn^{++} and Cr^{+++}. The results so far obtained for these two ions give $g \geqslant 2$. In the case of Mn^{++} all theories agree well with susceptibility measurements, and $g = 2$. For Cr^{+++} the original Hund theory gives g equal to 2·5, while calculation from the Laporte-Sommerfeld expression predicts a mean value of 1·4. Cr^{+++} is, therefore, another ion for which a direct determination of the gyromagnetic effect is required.

20. Magneto-resistance Effects. On the basis of their changes in electrical resistance when placed in a strong magnetic field, metals and alloys may be assigned to one, or the other, of two groups. Members of the first and more numerous group increase in resistance, whatever may be the relative directions of the current, i, and the applied field, H. Members of the second group increase in resistance if the current and the field are parallel, and decrease if they are perpendicular. All members of the second group are ferromagnetic, and no ferromagnetics occur in the first group.

---

* *Proc. Phys. Soc.*, **42**, 385 (1930).

† See Section 9.

‡ *Loc. cit.*

In the case of nickel,* the magnitude of the longitudinal magneto-resistance effect, i and H parallel, is nearly the same for all directions in a monocrystalline specimen, but with iron,† the longitudinal effect in monocrystals differs widely in magnitude for crystallographically different directions. The same applies to cobalt monocrystals.

Webster's experimental results for the longitudinal effect in a single iron crystal are shown in Fig. 48. The most remarkable fact is that, in spite of the enormous change of length (magnetostriction effect) for the (100) direction, there is practically no change of resistance. There is, however, a remarkable parallelism between the change of resistance for the other directions and their contraction in magnetostriction. Webster concludes that the change of resistance is caused by the distortion of some type of electron lattice, *i.e.*, the pulling away of the magnetic axes of the electrons from their normal cubic direction against the internal field. He has also shown that in the case of the transverse effect, i perpendicular to H, there is a small change of resistance, approximately proportional to the applied field. There is, in addition, a change depending for sign and magnitude on the directions of the current and magnetic field. This is the definitely crystalline effect, and it has the important property of vanishing whenever the magnetic field is parallel to a cubic axis, *i.e.*, whenever the magnetic condition of the iron is normal.

The effect in nickel along the (100) and (110) directions is exactly similar to that for iron, for the magnetically corresponding directions. In the case of the transverse effect, there is also a change of resistance with magnetisation along the (111) axis, but in this case it is a decrease of resistance. It seems to be due to electrical anisotropy of nickel, magnetised along its magnetic axis.

Another effect, closely related to the ferromagnetic properties.

---

* See Kaya, *Sci.* , **17**, 945 (1928).

† See Webster, *Soc.*, *A*, **113**, 196 (1926).

is the change of resistance with temperature. At temperatures above the Curie point nickel behaves like any other metallic conductor, in that the temperature-coefficient of resistance is constant for a considerable range of temperature. Immediately below the Curie point the resistance very quickly decreases with falling temperature.* The explanation of this phenomenon is, at present, somewhat uncertain.

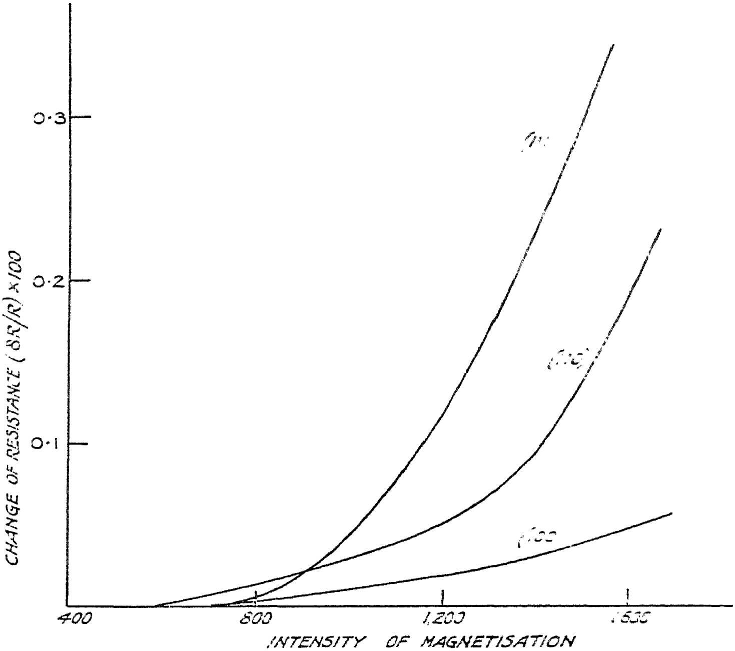


FIG. 48.—Magneto-resistance curves for single iron crystal.

21. Intense Magnetic Fields. Until recently, the use of electromagnets limited the field strength to approximately 50,000 gauss, whereas calculations show that the magnitude of the magnetic fields in the atom produced by moving electrons, even for the most loosely bound electrons, should be of the order of 1,000,000 gauss.

---

* See Gerlach, *Proc. Phys. Soc.*, 42, 431 (1930).

Now the magnetic field produced by a current in a coil of wire is proportional to the current, and the maximum field is really determined by the maximum heat permissible. Kapitza * conceived the idea of producing the magnetic field for such a short time interval that the coil has practically no time to overheat. In the first place he used specially made accumulators, of small capacity and small internal resistance. They were charged for a few minutes, and then discharged in 0·01 second, magnetic fields of 100,000 gauss being produced. Later, he replaced the accumulators by a single phase alternating current turbo-alternator. Such a type of machine, when short-circuited, can deliver very large impulses of current ; 50,000 kilowatts were actually obtained.

Although the time during which the intense magnetic field (300,000 gauss) persists is only 0·01 second, this interval is very long compared with that required for the magnetic phenomena, occurring in the atom, to establish themselves, and the loss of time in most experiments is compensated by gain in magnitude of the phenomenon observed.

The following phenomena in intense magnetic fields were investigated ; the change of resistance of metals, the susceptibility of certain metals, magnetostriction in metals and the α-ray tracks.

More recently Kapitza † designed a high frequency, damped sensitive type of balance by means of which it is possible to measure forces of a few grams in a time of the order of a hundredth of a second. By means of it he has found that the magnetisation of iron and nickel, after saturation, remains practically constant up to fields of 280 kilogauss. This result is in agreement with the Weiss-Langevin theory of ferromagnetism.

For gadolium sulphate a deviation from the linear law of magnetisation at the temperature of liquid nitrogen was observed,

---

* *Proc. Roy. Soc.*, *A*, **123**, 292 (1929).

† *Ibid.*, **131**, 224 (1931).

the magnitude of which agrees with the value given by the Langevin theory.

The magnetisation of bismuth for different crystal orientations at room temperature and at the temperature of liquid nitrogen has been measured, and found to be proportional to the magnetic field. From these results the dependence of the magnetic susceptibility on the temperature can be estimated for different crystal orientations.

22. Electrical Conduction in Intense Magnetic Fields. The apparatus used by Kapitza for the investigation of the electrical conductivity of metals is shown in Fig. 49. The magnetic field was produced for a short time interval in the coil A, in the opening of which was placed the Dewar flask C, containing the conductor B, whose behaviour in the magnetic field was to be studied. The current was sent through the conductor from the battery G, through the resistance H and the sector interruptor L, and was recorded by the oscillograph F. The make and break of the

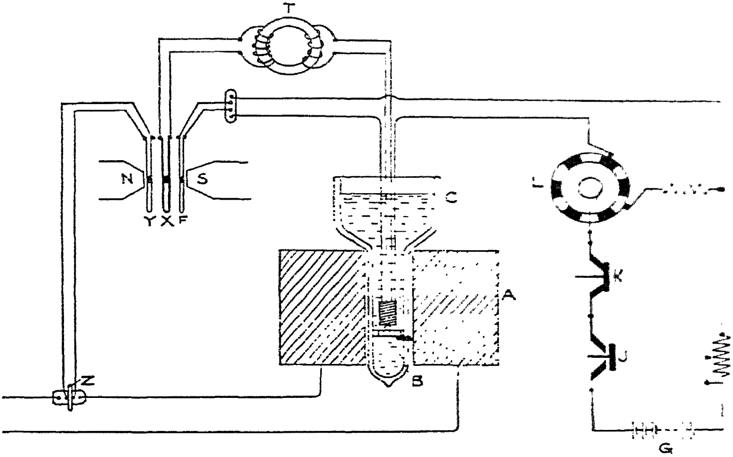


FIG. 49.—Experimental arrangement for measuring the variation of electrical conductivity in intense magnetic fields. (Kapitza.)

current through the conductor was produced by the two switches K, J. which were operated automatically, and timed with the current wave through the coil. The current through the coil was recorded by the oscillograph Y, and the potential difference across the conductor by a very sensitive oscillograph X.

The change of resistance was determined by measuring the ratio of the amplitude of the deflection of the potential oscillograph X with no field, to the amplitude when the field was on. The magnetic field was deduced from the amplitude of the curve drawn by the oscillograph Y, and the electromotive force induced by the variation of the magnetic field was eliminated by the sector L. For each metal, at a given temperature, two oscillograms were taken, one in which the field varied from 0 to 125 kilogauss, and the other from 0 to 300 kilogauss. Most of the metals were studied at three temperatures, room temperature (290° K), 193° K and 88° K.

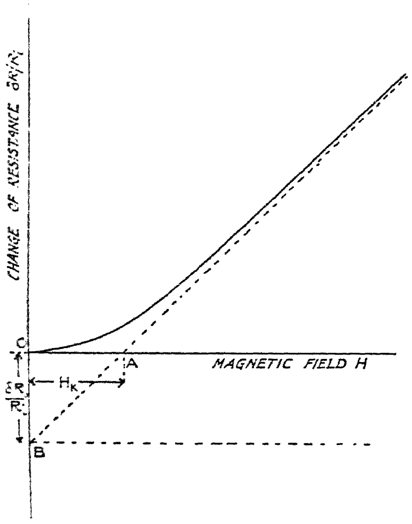


FIG. 50.—Critical magnetic field and additional resistance. (Kapitza.)

It was found that in every case with the weaker magnetic fields the relative change of resistance $\frac{\delta R}{R}$ was proportional to the square of the magnetic field, δR being the increase of the resistance, and R the resistance at the corresponding temperature. For stronger fields the increase of resistance follows a linear law, $\frac{\delta\mathbf{R}}{\mathbf{R}}$ being proportional to H. If an asymptote be drawn to the linear part of the $\frac{\delta\mathbf{R}}{\mathbf{R}} - H$ curve, it intercepts the axis of abscissæ at a magnetic field point H_K, as shown in Fig. 50. This value H_K is known as the *critical field*. The following formulæ were found to express the change of resistance within the limits of experimental error :

$$\frac{\delta\mathbf{R}}{\mathbf{R}} = \beta \frac{H^2}{3H_K}, \text{ for } H < H_K \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$\frac{\delta\mathbf{R}}{\mathbf{R}} = \beta \left(H - H_K + \frac{H_K{}^2}{3H} \right), \text{ for H} > H_K \quad . \quad . \quad (16)$$

where β is a constant depending on the tangent of the angle between the asymptote and the H axis. These two formulæ represent a continuous line, as it can easily be seen that at $H = H_K$ the curves will have the same value for the ordinate and also a common tangent. The linear part appears to be independent of the physical (crystalline) state of the metal, and to be related to the position of the element in the periodic table. Also the change of resistance depends on the direction of the field H with respect to the current in the conductor.

Typical curves are shown in Fig. 51, and the following results were obtained :

First Group of Elements, Li to Au. The value of β always diminishes from light elements to heavy ones but the changes in the value of $\delta\mathbf{R}/\mathbf{R}$ are small.

Second Group of Elements, Be to Hg. This group shows a large change of resistance even at liquid CO_2 temperature.

Third and Fourth Groups of Elements, Al to Th. Gallium has the smallest critical field, H_K, of all the metals examined. It appears to be only about 5,000 gauss.

Fifth Group of Elements, As to Ta. This group contains the two elements, bismuth and antimony, which are known to show a very large change of resistance in a magnetic field. Arsenic is similar to these two elements, *i.e.*, strongly diamagnetic. It must therefore behave in a similar manner.

Sixth, Seventh and Eighth Groups of Elements, Cr to Pt. In these groups Cr, Mo and W show a very considerable change of resistance, but the effect among members of the eighth group of elements is very small. Ferromagnetic metals exhibit a considerable change of resistance in weak magnetic fields, but comparatively small changes in strong fields.

Summarising his results, Kapitza finds that the increase of resistance is, at first, proportional to the square of the magnetic field, but as the intensity of the latter is raised, the increase of resistance becomes directly proportional to the field. This change from the square to the linear law takes place gradually after a critical field H_K has been exceeded which, for different substances, ranges from 5 to 250 kilogauss.

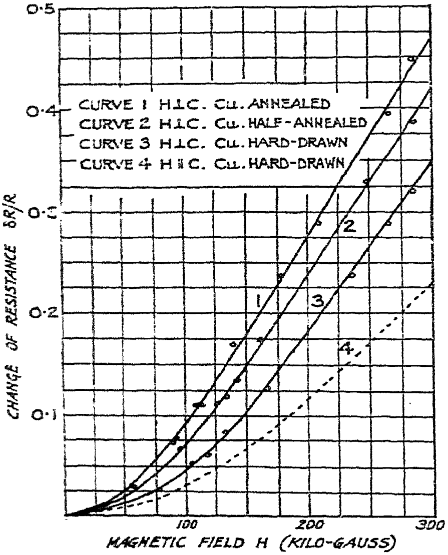


FIG. 51.—Change of resistance of copper in intense magnetic fields. (Liquid nitrogen temperature.)

He explains the phenomena by supposing that when the field is weak below the critical value, H_K, some internal phenomenon prevents the appearance of the linear law, which is the true law of change of resistance, and the latter is fully established only when the field is well above the critical value. He assumes an initial disturbance in the metal, produced by an internal magnetic field, distributed at random in the conductor.

When the external field is applied, the disturbance which causes the increase of resistance is due to the vectorial sum of the applied and randomly distributed fields, and the increase of resistance is proportional to this sum. As the disturbance produced by the external field becomes larger than that due to the internal field, we have the gradual approach to a linear law.

Kapitza considers that the total resistance observed in a metal is equal to the sum of $\mathbf{R}_i$, an *ideal resistance*, and $\delta\mathbf{R}_0$ an *additional resistance*. The former is constant for any given element at a given temperature, whereas the total resistance, **R**, may vary according to the physical and chemical state of the substance. To a first approximation, $\delta\mathbf{R}_0$ is not affected by temperature, but $\mathbf{R}_i$ diminishes rapidly with decreasing temperature, more so for the lighter elements than for the heavier ones. Kapitza suggests that his additional resistance and the *residual resistance* found by Kamerlingh Onnes are identical, and that the phenomenon of *superconductivity* consists in the disappearance of the additional resistance, the resistance of the conductor then being equal to its ideal resistance. According to this view, superconductivity is not a phenomenon confined only to certain metals, but can exist in all metals, only it is masked by the additional resistance, which does not disappear in most metals at low temperatures. The additional resistance from Kapitza's point of view has a different origin from the ideal resistance. It is mainly, if not entirely, produced by the structural and chemical imperfections of the metal in the conductor, whilst the ideal resistance depends on the temperature only, and in all metallic conductors probably disappears continuously, but very rapidly, as the metal is cooled, so that at a sufficiently low temperature it has immeasurably small values. This general theory cannot be applied, however, to arsenic, antimony and bismuth without some reservation.

Other measurements of the resistance of conductors in magnetic fields at low temperatures have been made by Meissner and Scheffers,* Schubnikow and Haas,† Meissner and Voigt,‡ and by Haas and Voogd.* Meissner and Scheffers found that their results for gold could be expressed by means of the formula :

---

* *Phys. Zeits.*, **30**, 827 (1929); **31**, .

† *Comm. Phys. Lab. Leiden*, No. 207.

‡ *Ann. d. Phys.*, **7**, 761 (1930); 892 (1931).

$\mathbf{R}_0$ is the resistance at 0° C., and $\delta\mathbf{R}$, the increase in resistance. This formula also becomes linear in form when H is very large, compared with H_K, and quadratic when H is small. The measurements of Kamerlingh Onnes and Tuyn † show that for lead in the superconducting state at 4·2° K., the resistance is of the order 10^{-10} of that at 273° K, whereas the value calculated by Meissner and Scheffers is only 10^{-4} of that at 273° K., a value 10^6 too large. Borelius ‡ has shown that with decrease of temperature the law of change of resistance gradually alters, ng a higher power of the temperature, T, as the latter At first the resistance varies as T^2, then for a shorter range as T^3, and for a still shorter range of temperature, as T^4. There are no evident reasons for supposing that this steady increase of power of the T's with decreasing ranges of temperature when the temperature is approaching the absolute zero. It thus appears impossible to extrapolate the resistance value at 4·2° K. with any degree of accuracy, but at the same time the istance must attain the very small values actually in the superconducting state.

Kapitza's suggestions with regard to the law of change of resistance in a magnetic field, and also with regard to superconductivity, form a definite working hypothesis, which permits a new and definite line of research to be instituted. Although much more experimental justification for the accuracy of the underlying assumption is still required, the experimental data of Meissner and Scheffers seem not only to strengthen the correctness of the underlying ideas of Kapitza's theory, but also to widen the range of their application.§

23. Theories of Ferromagnetism. Many attempts have been made to explain the stability of magnetisation, which distinguishes ferromagnetic materials from all others, by means of unitary magnets, arranged in a crystalline way. Some of these theories will now be considered.

---

* *Comm. Phys. Lab. Leiden*, No. 212.

† *Ibid.*, No. 198.

‡ *Zeits. f. Phys.*, 54, 807 (1929).

§ See Bethe, *Nature*, 127, 336 (1931).

Ewing's Theory. Ewing [*] postulated an extended group of identical molecular magnets, such magnets being centred at all the corners of a square-meshed plane net, with their axes parallel and in the plane of the net. As a randomly-directed magnetic field in the plane of the net is first increased from zero to a sufficiently high value, reduced to zero, and then increased in the opposite sense, the predicted behaviour of the magnetic moment of the aggregate is strikingly similar to the observed behaviour of the magnetic moment of a real piece of iron, held stationary and subjected to the same treatment. For a three-dimensional model Ewing supposed the square-meshed nets to be superposed as required, but although the models which he constructed exhibit the principal phenomena of ferromagnetism in a highly satisfactory manner, attempts to fix the length of an atomic magnet gave rise to serious difficulties. Ewing recognised that no single value of the ratio of the length of the magnet to the lattice constant could satisfy the experimental data. If the ratio is made practically equal to unity, the maximum stable deflection may be made as small as the narrow range of "elastic" magnetisation requires. Then, however, the intensity of the applied field, required to upset the initial arrangement, becomes much too great. To overcome this difficulty Ewing [†] shortened the magnet responsible for the intensity of magnetisation, introducing for its proper control a symmetrical group of magnets fixed in the atom, and also fixed with respect to the crystal space-lattice. This model then resembles others of recent date.

On his theory hysteresis energy-losses must be accounted for by the dissipation of magnetic potential energy, whenever sudden changes of the orientation of atomic magnets occur.

Peddie's Theory. Peddie [‡] considered the magnetic stability of co-directed magnetic doublets, arranged on a space lattice. He calculated the magnetic field at a lattice-point, due to equal doublets at all the other lattice-points of an infinite lattice. If this field coincides in direction with that chosen for the doublet axes, the arrangement is inherently stable, and the degree of stability is measured by the computed field intensity. If the computed field direction is not that of the doublet axes, an applied field, with a suitable component perpendicular to the doublet axes, is necessary and sufficient for stability. According to his assumptions, all changes of orientation of the atomic magnets are continuous, so that the theory makes no provision for that magnetic hysteresis which is the distinguishing feature of ferromagnetism. What it does explain is the difference in the direction of the intensity of magnetisation, corresponding to magnetic saturation, and the applied field. Peddie's theory is inapplicable for small values of the field.

---

[*] *Proc. Roy. Soc. Edinb.*, **47**, 141 (1927).

[†] *Proc. Roy. Soc.*, *A*, **100**, 449 (1922).

[‡] *Proc. Roy. Soc. Edinb.*, **47**, 165 (1927), and earlier papers.

Gans's Theory. Gans * assumes that the axes of the unitary magnets are arranged in space according to a general distribution function, which can be specialised to suit various initial conditions. His theory ignores the crystalline character of the medium, by postulating that the magnetisation shall always be parallel to the applied field. More recently † he has proposed a theory for the magnetisation of polycrystalline metals which includes more of the essential phenomena. Each crystallite is supposed to have a singular direction of easiest magnetisation and a sensibly rectangular hysteresis loop. The magnetisation curves and hysteresis loops, computed on assuming further that the distribution of unique directions of magnetisation in space is at random, agree very well with curves regarded as typical of well-annealed metal. He divides the effective field in each crystallite into three parts: the applied field, the field due to the combined action of remote parts of the specimen, and the field due to the adjacent crystallites. The direction and magnitude of the third component alone vary from point to point, so as to account for the different values of the applied field and of the average magnetisation at which discontinuities occur. He has succeeded in demonstrating the underlying diamagnetism of a ferromagnetic alloy—permalloy—in a field exceeding 8,000 gauss.

---

* *Ann. d. Phys.*, 63, 382 (1920).

† *Schrifter d. Königsb. gelehrten Ges. Naturwiss.*, 6, 2 (1929).

Mahajani's Theory. Mahajani * also makes the stabilising mechanism purely magnetic, and considers the unitary magnets to have linear dimensions comparable with interatomic distances. Two types of crystals are considered, *viz.*, iron with cubic structure and pyrrhotite with non-cubic structure.

Now in a crystal the internal, or molecular, magnetic field of Weiss is not, in general, parallel to **I**, the intensity of magnetisation, but its components $(H_M)_x$, $(H_M)_y$ and referred to the principal axes of magnetisation, are assumed by Weiss to be proportional to the components of **I** along these axes :

$$\begin{aligned}(H_M)_x &= m_x\mathbf{I}_x,\\ (H_M)_y &= m_y\mathbf{I}_y,\\ (H_M)_z &= m_z\mathbf{I}_z,\end{aligned}$$

where m_x, m_y, m_z are constants. But in a cubic crystal we should expect $m_x = m_y = m_z$, *i.e.*, magnetic isotropy in such media. Ferromagnetic cubic crystals are certainly not isotropic, so Webster † has suggested that these simple equations for $(H_M)_x$, $(H_M)_y$ and $(H_M)_z$ must be abandoned and more complicated forms substituted. Mahajani uses the expressions :

$$\begin{aligned}(H_M)_x &= m_x\,(a_1\mathbf{I}_x + a_3\mathbf{I}_x^{\,3} + a_5\mathbf{I}_x^{\,5} + \ldots),\\ (H_M)_y &= m_y\,(a_1\mathbf{I}_y + a_3\mathbf{I}_y^{\,3} + a_5\mathbf{I}_y^{\,5} + \ldots),\\ (H_M)_z &= m_z\,(a_1\mathbf{I}_z + a_3\mathbf{I}_z^{\,3} + a_5\mathbf{I}_z^{\,5} + \ldots),\end{aligned}$$

considering two terms for cubic crystals, and one for non-cubic crystals. The quantities derived from experiment are the maximum values of the molecular field, *i.e.*, $(H_M)_x$ for **I** along the x-axis, etc. In Webster's experiments these are of the order 500 gauss, and to satisfy this, Mahajani assumed the radius of his Weber element to be about 2×10^{-9} cm., a reasonable value for an electronic orbit.

He makes one improbable assumption, *viz.*, that the atomic magnets, associated with one of the two simple cubic space-lattices, into which the body-centred cubic space-lattice of iron may be decomposed, are always all parallel to one line, those associated with the other simple cubic-lattice to another. Since the points of these two lattices ought to be crystallographically equivalent, there is no reason for this postulate on physical or chemical grounds. The quantitative success of the theory does not depend, however, upon this assumption.

---

* *Phil. Trans.*, **228**, 63 (1929).

Soc., *A*, **107**, 496 (

Akulov's Theory. In his treatment of ferromagnetic crystals Akulov * considers not only the torque exerted upon each atomic magnet by the whole array, but also the anisotropic cohesive forces which arise when the magnets are co-directed in various crystallographic directions. His theory agrees with the magnetostriction observed in single crystals by Webster † and by Honda and Mashiyama.‡ It ignores hysteresis, and can only apply with rigour to relatively intense magnetisations where the width of the hysteresis loop becomes negligible. If $\mathbf{I}_p$ is the intensity of magnetisation parallel to the applied field H_A, Akulov measures the area between the $\mathbf{I}_p$ axis and the $\mathbf{I}_p$—H_A curve, up to a line drawn parallel to the H_A axis at a distance $\mathbf{I}_s$ therefrom, where $\mathbf{I}_s$ is the saturation value of $\mathbf{I}_p$. This area changes as the direction of H_A is rotated about in a chosen crystallographic plane containing two axes, for which the direction of $\mathbf{I}$ is parallel to H_A. The curve connecting the area, thus measured, with the azimuth of H_A is closely reproduced by the theory.

In extending his theory to lower field intensities Akulov assumes, contrary to custom, that the atomic magnets point in all possible directions when the crystal is unmagnetised, *i.e.*, their orientations are in statistical disorder. He also assumes spatial quantisation with respect to the applied field, H_A. The local magnetic field arising from neighbouring atoms is thus ignored. He also supposes that there are only two stable orientations for each magnet, one parallel to H_A, and the other anti-parallel. Starting from these postulates he arrives at the following results for magnetisation. If the areas between $\mathbf{I}_p$—H_A curves are taken. not up to $\mathbf{I}_s$ as before, but up to any arbitrary value, $\mathbf{I}_p$, the curves $\int_0^{I_p} H_A d\mathbf{I}_p$—$\phi$, where ϕ is the azimuth of H_A, are derivable from the curve $\int_0^{I_s} H_A d\mathbf{I}_p$—$\phi$, by a mere change of scale. If **I** is maintained constant in magnitude by a suitable choice of H_A, the theory predicts that as the direction of **I** is allowed to vary, $H_A\mathbf{I}$ is the same function of the direction of **I** for all values of **I**. Both of these predictions have been verified experimentally. Also, by means of the theory, the value of $H_A - (H_A)_0$ may be calculated where H_A and $(H_A)_0$ are, respectively, the magnitude of the applied field in a random direction, and that in a principal direction of magnetisation, corresponding to a given value of $\mathbf{I}_p$. The predicted values agree with the experimental ones.

---

* *Zeits. f. Phys.*, **52**, 389 (1928) ; **54**, 582 ; **57**, 249 (1929) ; **59**, 254 (1930) ; **69**, 78 (1931).

† *Proc. Roy. Soc. A*, **109**, 570 (1925).

‡ *Sci. Rep. Tohoku Imp. Univ.*, **15**, 755 (1926).

Akulov's theory is very successful in dealing with those ferromagnetic phenomena which are important in magnetic fields of strength greater than the coercive force. Under these conditions we can imagine, as a first approximation, that the whole array of atomic magnets wheels together under the action of an increasing magnetic field, constant in direction.

Becker's Theory. Becker * assumes distortion of the space-lattice, and by means of this assumption correlates magnetic properties with mechanical strains. In this respect he follows many workers who have concluded that mechanical constraints are the chief, if not the only, source of ferromagnetic stability and resulting hysteresis.

As an approximation, Becker postulates that the direction of **I** lies always in the plane determined by the direction of H_A and that of the strain-determined spontaneous magnetisation, $\mathbf{I}_0$. The form and dimensions of the regions within which $\mathbf{I}_0$ may be considered constant in direction are undetermined. If the regions contain but a few atoms each, the stable orientation of each atom is fixed mechanically by the distances and orientations of its nearest neighbours.

---

* *Zeits. f. Phys.*, **62, 253 (1930).**

A magnetisation curve, appropriate to crystalline metal, is derived by Becker on the assumption that the local strains, which fix in each region the direction of its initial magnetisation, are large in comparison with magnetostriction strains, so that the change in the elastic energy, due to rotating the magnets in any region, may be negligible. The degree of strain in each region, and the direction of magnetisation which the strain stabilises, together fix a critical field, different for different directions of H_A, at which discontinuous changes in $\mathbf{I}_p$ take place for sufficiently wide ranges in $\mathbf{H}_A$. In this manner Becker accounts for the coercive force, remanent magnetisation, a single Barkhausen discontinuity, and a hysteresis energy loss per cycle for each region. An averaging over all the regions leads to the kind of hysteresis loop usually found in practice.

On this theory the maximum coercive force, explicable by purely elastic strains, is 140 gauss, a good approximation to experimental facts. The coercive force depends directly upon the numerical factor which determines the magnitude and sign of the longitudinal magnetostriction. The wide variation of remanent magnetisation in different materials is attributed to the wide differences in the distribution function for the directions of the spontaneous magnetisation in the unmagnetised specimen.

Elastic stress on the specimen, as a whole, will be expected to alter the coercive force and the remanent magnetism in the general way in which experiment shows that they do vary. It is interesting to note in this connection that Ewing visualised the importance of elastic strain in changing the orientation of the magnets in his original model. He did not, however, imagine an initial strain which Becker postulates.

Heisenberg's Theory. The classical and older quantum theories could give no satisfactory explanation of the internal, or intrinsic, field phenomena. Heisenberg* has now shown how these may arise from a type of interaction, characteristic of the newer quantum mechanics. Consider an ideal ferromagnetic substance consisting of an aggregate of atoms, each containing one electron free to change its orientation, the remainder of the atom having no magnetic effect. Each atom can interact with its neighbours. For two hydrogen atoms at a given distance apart, there are two possible energy states, in one of which the electronic orbits are parallel and in the other anti-parallel. The difference in energy between these two states far exceeds that due to the purely magnetic interaction. Similarly in the ideal ferromagnetic, the energy will depend indirectly on the mutual orientation of the electronic orbits in neighbouring atoms. The electron interchange is not an actual transfer of an electron from one atom to another, and *vice-versâ,* as the word interchange might seem to imply, but only a mutual effect of two electrons, one in atom A, say, and one in atom B, by which the states, permissible to each, are reduced in number, and in particular the state of mutual parallelism of electronic orbits is made more probable.

---

* *Zeits. f. Phys.*, **49**, 619 (1928); **69**, 287 (1931).

A complicated statistical treatment is applied to the crystal as a whole, and expressions are obtained for the Curie-point and the variation of magnetisation with temperature, in terms of the interchange interaction, and the number of neighbours of each atom. As a first approximation, the expressions obtained agree with those from the Weiss theory, and so are in agreement with experiment ; the detailed expressions, however, are unsatisfactory, and indicate that some modification in the treatment is necessary.

Slater * has made important progress in discovering a reason for the unique position of iron, cobalt and nickel as ferromagnetic elements, by importing into the theory the idea that the probability of interaction increases as the ratio of interatomic distance to radius of incompleted electron shell increases.

Other Theories. Other theories have been proposed by Dorfman and his colleagues † and by Dillinger.‡ Powell § has explained the facts with regard to the magnetisation of single ferromagnetic crystals by taking into account the magnetic interaction between each electron and the atom to which it belongs. Fowler and Powell * have amplified this theory.

---

* *Phys. Rev.* **35,** 509 ; **36,** 57 (1930).
† *Zeits. f. Phys.*, **54,** 277 (1929) ; 289 (1929).
‡ *Phys. Rev.*, **33,** 398 (1929).
§ *Proc. Roy. Soc.*, *A*, **130,** 167 (1931).

BIBLIOGRAPHY

DARROW. *Bell System Technical Journal*, 6, 295 (1927).
McKEEHAN. *Reviews of Modern Physics*, 2, 477 (1930).
PEDDIE. "Molecular Magnetism."
Proceedings of the Physical Society, 42, 355 (1930).
STONER. "Magnetism and Molecular Structure."
WALL. "Applied Magnetism."
WEISS and FOËX. "Le Magnétisme."
WILLIAMS. "Magnetic Phenomena."

---

* *Camb. Phil. Soc. Proc.*, 27, 280 (1931).

CHAPTER VIII

ELECTRICITY

1. Electric Moment and Dielectric Constant. Faraday concluded that the particles of an insulating dielectric, whilst under induction, may be compared to a series of small insulated conductors, and further, he assumed that each of these conductors consisted of a single molecule which could be polarised as a whole. When this polarisation occurs, one side of the molecule acquires a positive charge and the opposite side a negative one of equal magnitude, so that the molecule as a whole is neutral. This pair of charges may be regarded as forming a small doublet, or *dipole*, and for any dielectric we have the Clausius-Mossotti relation :

$$\frac{K-1}{K+2}\cdot\frac{1}{d} = \textit{constant},$$

in which K is the dielectric constant and d, the density. The approximate constancy of the expression, called the *polarisation*, was established for substances of low dielectric constant, but in many cases, particularly those of high dielectric constant, the polarisation was found to vary greatly with the temperature.

Debye * has applied to dielectrics a treatment analogous to that used by Langevin in discussing paramagnetism, assuming that a molecule may contain a permanent doublet of moment μ, which causes the molecule to become oriented in an electric field, so that the effect of the doublet, induced by an applied field, is then superimposed upon that of the permanent doublet. The orientation of the molecule containing the doublet is opposed by thermal agitation of the molecules which, of course, varies with the temperature. Debye has proposed the following formula

* **“ Handbuch der Radiologie ” (1925).**

for the polarisation of a gram-molecule of a substance *i.e.* the *molar polarisation*, P,

$$P = \frac{K-1}{K+2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\gamma + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT},$$

where M is the molecular weight, N, the number of molecules per gram-molecule, *i.e.* $6{\cdot}061 \times 10^{23}$, γ, the *molecular polarisability*, or the moment of the doublet induced on a molecule by a field of strength unity, k, the molecular gas constant, *i.e.*, $1{\cdot}372 \times 10^{-16}$, T, the absolute temperature; μ is the mean component of the moment per molecule in the direction of an internal field of unit strength. As T is the only variable on the right of the above equation, it is evident that when the molecule contains no permanent doublet ($\mu = 0$) the second term on the right-hand side is missing, and the equation becomes equivalent to the Clausius-Mossotti expression, which takes account only of doublets induced in molecules. However, when the molecule is unsymmetrical electrically in that it contains a permanent doublet, polarisation is a linear function of $1/T$, and the second term on the right-hand side of the equation may be much larger than the first.

The expression for P may be written in the form :

$$P = a + \frac{b}{T},$$

where
$$a = \frac{4\pi N}{3}\gamma\,;\; b = \frac{4\pi N\mu^2}{9k}.$$

In the derivation of this equation on the basis of classical mechanics, it is necessary to suppose that in the absence of an external field, the molecules are oriented at random. The application of the principle of quantised orientation to the problem led to an equation of the same general form, but with a different coefficient for the second term.* However, the applications of the new quantum mechanics to simple polyatomic molecules have given equations from which results, practically identical with those of the Debye equation, may be obtained.*

---

* See Pauli, *Phys. Zeits.*, **6**, 319 (1921) ; Pauling, *Proc. Nat. Acad. Sci.*, **12**, 32 (1926).

When the molecules are not exactly free to orient in an applied field, the equation cannot be expected to apply. For gases, the dielectric constants of which are close to unity, simplification may be effected by setting $K + 2 = 3$. The validity of this simplified equation has been established experimentally by Jona,† Zahn,‡ Sänger,§ and others.||

Zahn, for example, used an improved heterodyne null-method of measurement; the beats between two high-frequency oscillations from separate valve generators were adjusted to the frequency of a tuning fork, the small change of capacity due to the introduction of the gas being compensated by a considerable change in a large capacity placed in series with the gas condenser.

Now, according to Debye's theory, the dielectric constant of a gas may be written in the form:

$$(K - 1)\,vT = AT + B$$

where v is the specific volume, referred to normal temperature and pressure, occupied by 1 c.c. of an ideal gas, A, a constant which represents the electric polarisation due to induced distortion in a molecule, and B, a constant which is a function of the orientation polarisation, and is proportional to the square of the electric moment of the molecule ($\mu^2 = 1{\cdot}198 \times 10^{-36} B$). If $(K - 1)vT$ is plotted against values of T, a straight line is obtained of slope A and intercept B, the latter determining μ. For gases of symmetrical structure $B = 0$, and the straight line passes through the origin of co-ordinates.

Some of the results obtained by Zahn and Zahn and Miles ¶ are in Table XI.

---

* See Kronig., *Proc. Roy. Acad. Sci.*, 12, 488 (1926); Mensing and Pauli, *Phys. Zeits.*, 27, 509 (1926); Manebuck, *Phys. Zeits.*, 27, 563 (1926); Van Vleck, *Phys. Rev.*, 30, 31 (1927).

† *Phys. Zeits.*, 20, 14 (1919).

‡ *Phys. Rev.*, 27, 455 (1926).

§ *Phys. Zeits.*, 28, 455 (1927).

|| See Smyth and Zahn, *Journ. Amer. Chem. Soc.*, 47, 2501 (1925); Weigt, *Phys. Zeits.*, 22, 643 (1921).

¶ *Phys. Rev.*, 32, 497 (1928).

TABLE XI. THE ELECTRIC MOMENT OF THE MOLECULES OF GASES.

Gas	Values of $A \times 10^6$.	Values of B.	Values of $\mu \times 10^{18}$ (Electrostatic units.)
HCl . .	1,040	0·895	1·03
HBr . .	1,212	0·52	0·79
HI . .	1,856	0·12	0·38
C_2H_2 . .	1,334	0	0
C_2H_4 . .	1,444	0	0
C_2H_6 . .	1,501	0	0
C_4H_8 . .	2,694	0·115	0·37
N_2 . .	580	0	0
CO_2 . .	958	0·003	0·06
NH_3 . .	768	1·74	1·44
SO_2 . .	1,433	2·167	1·61
H_2S . .	1,223	0·722	0·93
CO . .	670	0·007	0·10
CS_2 . .	2,798	0·089	0·32

The moment of a permanently polarised molecule might be measured as in Gerlach and Stern's experiment on the magnetic deviation of atomic rays. Clark * proceeded on simpler lines. He used a narrow beam of molecules in the path of which was placed a wire at right angles to the direction of the beam, and maintained by a battery at a potential considerably greater than that of a co-axial cylinder surrounding it. The electric field outside the wire could therefore be calculated. As the wire is in the beam, some molecules will pass on either side of it, and from the resulting deflection the electric moment of the molecule can be calculated. The value found for As_2O_3 was $1{\cdot}3 \times 10^{-19}$ E.S.U. This is of the right order of magnitude as predicted by the theory of permanent dipoles put forward by Debye, and further, the moment did not appear to be influenced by the strength of the field; it is therefore a permanent characteristic of the molecule. The results also showed that there was no definite orientation of the molecules,

---

* *Proc. Roy. Soc.*, *A*, **124**, 689 (1929).

save parallel, or antiparallel, to the field, but a distinction between parallel and antiparallel orientation could not be made in this experiment.

Keyes and Kirkwood [*] have recently determined the dielectric constant of CO_2 and NH_3 at different temperatures and pressures, Fucks [†] has measured the value of the constant of some organic vapours, and McLennan, Jacobsen and Wilhelm [‡] that of liquid nitrogen, argon, methane and nitrous oxide.

In liquids the molecules are so close together that large doublets attract one another, forming complex molecules, or restricting one another's freedom of motion. The first term of Debye's equation is little affected by the mutual action of the molecules, but the second term is decreased owing to lack of freedom of the molecules. The inapplicability of the equation to certain dipole liquids was shown by Smyth [§] and Lange.[||]

Debye's equation has also been developed in the more general form :

$$\frac{K-1}{K+2}\,\frac{M}{d} \qquad \frac{4\pi N}{3}\cdot \quad 1+ \qquad \cdot\frac{\mu^2}{3kT},$$

in which ω is the frequency of the applied alternating field and ω_0, a characteristic frequency, equal to $kT/4\pi a^3\eta$, a being the molecular radius and η, the coefficient of viscosity of the dielectric. Under ordinary conditions of measurement ω is so small in comparison with ω_0 that ω/ω_0 is negligible, and the equation becomes identical with the simpler one already discussed, so that the dielectric constants of gases and of liquids of normal viscosity are independent of the frequency down to very short wave-lengths. As the frequency is increased, until the wave-length is but a few centimetres, the value of ω/ω_0 becomes appreciable, and rapidly increases with decreasing wave-length. Mizushima,[¶] measuring the dielectric constants of a number of alcohols at wave-lengths 3·08, 9·5 and 50 metres, respectively, has found that at a given temperature, the dielectric constant begins to decrease at a shorter wave-length the larger the molecule, and for a given molecule the temperature at which the decrease begins is higher the shorter the wave-length.

---

[*] *Phys. Rev.*, **36**, 754, 1570 (1930).

[†] *Zeits. f. Phys.*, **63**, 824 (1930).

[‡] *Trans. Roy. Soc., Canada*, **24**, 37 (1930).

[§] *Phil. Mag.*, **45**, 849 (1923).

[||] *Phys. Zeits.*, **33**, 169 (1925).

[¶] *Sci. Papers, Inst. Phys.-Chem. Research, Tokyo*, **5**, 201 (1927).

Measurements of the variation of dielectric constants with frequency have also been made by Boch,* Tear,† Nichols and Tear ‡ and Johnstone and Williams.§

An explanation of this effect may be summarised as follows: the polarisation due to orientation will decrease as the frequency of the field is increased, and will vanish when the frequency becomes sufficiently high. Under the latter conditions the dielectric constant of the medium is equal to n^2, where n is the refractive index. The transition from orientation to pure distortion occurs in the frequency region ω_c, determined by $\omega_c\tau =$ constant, where τ is defined by Debye as the *time of relaxation* ‖ of the liquid, *i.e.*, the time required for the molecules to assume random distribution after the electric field is cut off. Debye assumes the molecules to be spheres, the dilution to be infinite, the *inner friction*, *i.e.*, the friction experienced by a molecule as it moves through a liquid, to be the same as the measured viscosity, and the Stokes's formula for inner friction to hold. By the aid of the Einstein theory of Brownian motion, he derives a partial differential equation defining the distribution function of the dipole moments when affected by a field of variable frequency, and shows ¶ that:

$$4\pi\zeta^{\sim 3}$$

where a is the radius of the molecule and ζ, the inner friction coefficient.

If the period of the external field is greater than τ, the dielectric constant of a dipole liquid should have a high constant value, but as the period of the field approaches τ, there will be a rapid decrease in the dielectric constant, and for very high frequencies it will become equal to the square of the refractive index of the substance. The effect is thus analogous to anomalous dispersion in optics, and has been demonstrated in polar liquids by several investigators.*

---

* *Zeits. f. Phys.*, 31, 534 (1925).

† *Phys. Rev.*, 21, 600 (1923).

‡ *Ibid.*, 21, 587 (1923).

§ *Ibid.*, 34, 1483 (1929).

See Section 9.

"Polar Molecules" (1929).

When a substance is solid and the molecules are unable to orient in an applied field, the second term of Debye's equation should disappear. Substances which possess dipoles in their molecules normally show a great fall in polarisation on solidification, after which there is little variation with temperature. However, Errera † reports that the dielectric constants of a number of substances containing electric moments, when measured at wave-lengths of some hundreds of kilometres, show little decrease on solidification, and it is only when the wave-length is reduced to about 1 km., or the temperature of the solid lowered far below its freezing-point, that the dielectric constant decreases to a value which would make the second term of the equation negligibly small. This seems to indicate that the molecules of a solid near its melting point possess sufficient mobility to turn slowly in an alternating field.

The electric moment of a molecule is not a mere mathematical quantity, arbitrarily adjusted to make an equation fit experimental data, but a definite physical entity, dependent upon molecular structure. The dependence of the dielectric constant upon other properties of the material may be summarised in the statement that it depends upon the number and mobility of the electrons per unit volume of material, and when the molecules contain electric doublets, to a much greater extent upon the size and arrangement of the doublets in the molecules, the freedom of the molecules to orient, and the number of molecules per unit volume.

2. Atmospheric Electricity. There exists always and every-where a permanent electrical potential difference between the earth and the air, which varies with time and place but has an average value of 100 to 300 volts per metre. The mean conductivity of the air is about 2×10^{-4} electrostatic units, and the mean intensity of the vertical atmospheric current amounts to 2×10^{-16} ampere.

---

* See Lange, *Zeits. f. Phys.*, **33**, 169 (1925); Williams and Krchma, *Journ. Amer. Chem. Soc.*, **49**, 1676, 2408 (1927); Williams and Ogg, *ibid.*, **50**, 94 (1928); Errera, *Phys. Zeits.*, **27**, 764 (1926).

† *Journ. Amer. Chem. Soc.*, **50**, 1547 (1928).

Data for high altitudes are extremely scanty but Wiegland * and Idrac † both report altitude observations in which the electric field drops from 100 volts per metre at the earth's surface to nearly zero at 8 km., and then in the region between 8 and 12 km. rises in such a way as to indicate an excess of negative ions, followed by an excess of positive ions between 12 and 19 km., where the electric field has again decreased to zero.

The more important agencies which may conceivably produce ionisation in the upper atmosphere of the earth are the ultra-violet light, α and β particles, all of solar origin, the penetrating radiation of cosmic origin and the ionising radiations from terrestrial sources. The last mentioned may perhaps be ruled out immediately, because of the fact that the ionisation in the lower atmospheric strata increases rapidly with altitude for the first few kilometres. The penetrating radiation produces but few ions, about 1·4 per c.c. per sec. at the surface of the earth, and its ionisation effect at high levels may be expected to be very small. Hypotheses of α and β particles from the sun must be regarded as tentative in the extreme, and it may be stated that no phenomena have yet been discovered which point unmistakably to the existence of such particles. There remains the ultra-violet light from the sun as deserving first consideration. This produces electron and ion densities in the high atmosphere, in agreement with those inferred from the propagation of wireless waves. Further, because the question of the ionisation of the high atmosphere is merely a part of the larger subject—the entire physics of the atmosphere—the ultra-violet light theory enters into the explanation of the aurora, the light of the night sky and the production of ozone. The possible effects of the various ionising

---

* *Ann. d. Phys.*, **66**, 261 (1921).

† *Comptes Rendus*, **182**, 1634 (1926).

agencies have been considered by Swann,* Chapman and Milne,† Chapman,‡ Elias,§ Lassen,|| Benndorf,¶ and others.

The facts of terrestrial magnetism and their physical interpretation furnish clues to the ionisation below 190 km. Gunn** showed that long free-paths ions in a magnetic field were diamagnetic, and from this he evolved a theory of the quiet day solar diurnal variations in the earth's magnetic field. He accounted for the prominent features of the solar diurnal variation on the assumption that the diamagnetism of the atmosphere, due to the ions, was a maximum directly underneath the sun and fell off approximately with the cosine of the angular distance from high noon, becoming, at night, about 1/10th, or less, of its noon maximum value. At the noon maximum the theory required, in a column of the atmosphere, 1 sq. cm. section, 5×10^{16} ions at a temperature of 300° K., or, since the diamagnetism of an ion depends on its kinetic energy, and hence on the temperature, 3×10^{16} ions at 500° K., or $1{\cdot}5 \times 10^{16}$ at 1,000° K. Below 150 km. the free paths are so short that the ions do not contribute to the diamagnetism. Therefore, the ions were taken to be mainly in the levels from 150 to 180 km., although the exact height to which they extended was not very important as long as it was not too great, say, below 200 km. Maris †† had previously shown that the noon-day temperatures in the atmosphere, above 100 km., were probably 300° K., or greater, and Maris and Hulburt ‡‡ found that the temperatures might be as high as 1,000° K. Maris's tables of the molecular densities in the upper atmosphere indicated that the 150 km. levels of the atmosphere, because of the expansion of the lower levels of the atmosphere due to the heat of the sun, moved upward about 20 km. in the morning, descending again in the afternoon.

---

* *Terr. Mag. and Atmos. Elect.*, **21**, 1 (1916).
† *Roy. Met. Quart. Journ.*, **46**, 357 (1920).
‡ *Ibid.*, **52**, 225 (1926).
§ *Zeits. f. Hochfreq. Technik.*, **26**, 66 (1926).
|| *Ibid.*, **28**, 109, 139 (1926).
¶ *Phys. Zeits.*, **27**, 687 (1926).
** *Phys. Rev.*, **32**, 133 (1928).
†† *Ibid.*, **32**, 133 (1928).
‡‡ *Ibid.*, **33**, 412 (1929).

Hulburt,[*] from the laws of recombination of the ions and of diffusion and drift of the ions in the earth's magnetic, gravitational and electric fields, calculated the distribution of the ions over the earth. His results agree with Gunn's theory. The gravitational drift currents due to the ions are found to flow mainly along the parallels of latitude in the following way: (1) a current sheet in the daylight hemisphere flowing eastward in the levels above 150 km. which, at sunrise and sunset longitudes, divides into two sheets; one of these flows westward on the day side of the earth underneath the first current sheet in the levels below 150 km., and the other continues eastward around on the night side of the earth. The current is mainly, *i.e.*, 4/5ths, between the 40th parallels of latitude north and south, and falls to lower values at the higher latitudes. The total currents in the three sheets are about $1{\cdot}16 \times 10^7$, $8{\cdot}7 \times 10^6$ and $2{\cdot}9 \times 10^6$ amperes, respectively. The east and west daytime current sheets subtract from each other leaving, in effect, an eastward current of about $2{\cdot}9 \times 10^6$ amperes flowing round the earth all the time. This causes a magnetic field, agreeing in magnitude and type with that obtained by Bauer[†] in his 1922 analysis of the magnetic field of the earth of external origin. The current sheets are not of the type required by Chapman's drift current theory[‡] of the diurnal magnetic variation. As a result of the drift currents, the sunset longitude of the earth is at a potential approximately 2,000 volts above that of the sunrise longitude. This electric field, combined with the earth's magnetic field, causes the ions and electrons on the night side of the earth to drift upward with velocities between 100 and 200 cm. per sec. The ions and electrons move into regions of lower pressure, and therefore do not recombine as fast as they would at higher pressures. The upward drift of the ionisation causes a rise of the Kennelly-Heaviside layer which is, partially at least, compensated for by the fall due to the cooling and contraction of the atmosphere at night, but is complicated by the diffusion of the ions. The night-time rise of the layer, observed in experiments with wireless waves, may be a genuine rise, or an apparent one, due to the delayed group velocities, or to other causes.

---

[*] *Phys. Rev.*, **34,** 1167 (1929).

[†] *Terrest. Mag.*, **28,** 1 (1923).

[‡] *Loc. cit*

3. Ozone in the Atmosphere. Closely connected with the ionisation in the atmosphere is the presence of ozone, and since this gas absorbs ultra-violet light of certain wave-lengths, the intensity of this light reaching the earth from the sun depends upon the amount of ozone in the atmosphere ; the intensity is measured photographically, and consequently the amount of ozone through which the light has travelled, can be found. This is expressed as the thickness of a layer of pure gas at normal temperature and pressure ; it varies about a mean value of approximately 3 mm. in Europe.

The height of the ozone layer can also be deduced. Dobson * puts the average height at about 50 km., which probably represents the " centre of gravity " of the layer.

The ozone is a minimum in the tropics ; it is a maximum in Arctic regions after the winter night, and decreases rapidly as the sunlight becomes stronger. From this it is concluded † that the amount of ozone produced by sunlight is relatively small (perhaps about 2 mm.), and there must be some other source of supply. The origin may possibly be found in the aurora, or some associated phenomenon of unknown nature. The amount of ozone is related to magnetic conditions in the sense that high ozone values tend to occur at times of magnetic disturbance, a marked auroral display being always accompanied by a magnetic storm. Nevertheless, the aurora is situated at a height of 100–500 km., far above that found for the ozone layer.

Fabry ‡ has calculated that there are 10^{19} molecules of ozone in a column of the atmosphere 1 square centimetre in cross-section.

4. Thunderclouds. Wilson § has shown that the potential gradients below thunderclouds, which generally reach values of the order of 10,000 volts per cm., are much more often negative than positive. He concludes that a thundercloud is bipolar, the positive charge tending to be above the negative charge, the preponderance of the negative potential gradients below thunderclouds being due, primarily, to the negative charge on a cloud being nearer the ground than the positive charge. The prevailing positive charge found on the rain is not the cause but the result of the negative potential gradient. The rain intercepts and returns to the earth a portion of the charge carried down by the stream of positive ions, which are being driven up by the negative potential gradient.

---

* *Nature*, **127**, 668 (1931).

† See Chalonge and Götz, *Comptes Rendus*, **188**, 704 (1929).

‡ *Proc. Phys. Soc.*, **39**, 1 (1926).

§ *Journ. Frank. Inst.*, **208**, 1 (1929). Watt has reviewed the theories of thunderstorms, *Roy. Meteorolog. Soc. Journ.*, **57**, 133 (1931).

Suppose that small particles in a cloud, which fall only slowly relatively to the air, are positively charged, while the larger drops which fall with considerable velocity through the air are negatively charged. Such a cloud, originally neutral, will at once begin to acquire a positive charge at the top and a negative one at the bottom, through the relative vertical motion of the two classes of carriers. The two equal and opposite charges, thus accumulating at the top and bottom, may be separated by a great thickness of neutral cloud. An electric field is developed within the cloud which tends to hinder negatively-charged drops from falling and positively-charged particles from being carried up by the air stream. There comes a stage where a balance is reached, and no further increase in the field results, the dissipation of the upper and lower charges by ionisation currents increasing as the charge increases. On the other hand, the field may reach the sparking limit before such a balance can be attained, and then we have the lightning flash. The dissipation from the upper and lower charges will not generally be equal, and in this way the cloud may acquire a net charge, positive, or negative.

Now the average magnitude of the electric moments destroyed by the discharges within the thundercloud is about 10^{16} electrostatic units-cubic millimetres, or 30 coulombs-kilometres. The intensity of the electric field required to produce a discharge, in the presence of drops of the size to be expected in thunderclouds, is 10,000 volts per cm., or 33 electrostatic units.

Suppose that the effective portion of the cloud has horizontal upper and lower limits. The electric moment, M, is equal to the product of the charge per unit area, the area, and the vertical thickness of the cloud, *i.e.*, $\frac{F}{4\pi}$ times the volume, where F is the magnitude of the field required to cause discharge. The volume required for the production of an electric moment of 10^{16} electrostatic units is found, in this way, to be 4 cubic km. The electrical energy stored in the cloud, and dissipated at each lightning flash, is $\frac{1}{2}MF$. If we put $M = 10^{16}$, and the maximum field $= 33$ electrostatic units, the energy of the lightning discharge $=1{\cdot}6 \times 10^{17}$ ergs, or $1{\cdot}6 \times 10^{10}$ joules. The value found for the maximum potential difference in clouds depends on the vertical thickness, *i.e.*, the distance through which the maximum field F extends. If we take this height as 1 km., and a field of 10,000 volts per cm. extends through this distance, the whole potential difference is 10^9 volts, *i.e.*, 1 million kilovolts.

There is now strong evidence that both by continuous discharge and by lightning flashes an upward electric current is maintained both by shower and thunder clouds, and that this exceeds the oppositely directed current brought down by rain. Wilson holds that shower and thunderclouds are the main agents in the maintenance of the negative charge on the earth in fine weather, and that they act as electric generators which remove positive electricity from the earth and supply it to the conducting upper atmosphere, by which it is distributed over the whole earth. The upper atmosphere is thus maintained at a potential of one million volts. If we take the estimate, $1{\cdot}7 \times 10^{10}$ joules, for the energy of a lightning flash, and assume that there are 100 flashes per second (an estimate) the total rate of dissipation of energy is $1{\cdot}7 \times 10^{12}$ watts, *i.e.*, more than 1,000 million kilowatts per second.

An important factor in the electric power of thunderclouds is the electromotive force, since this is greater than that we are likely to attain by artificial means. Wilson obtained the value 10^9 volts. The main interest in having available sources of energy reaching the magnitudes attained in thunderclouds would consist in the possibility of giving to the electrons, or the atomic nuclei, energies enormously exceeding those associated with α and β particles from radioactive substances.

The process of imparting energy to electrons must always go on naturally in thunderclouds on a scale we cannot hope to imitate in the laboratory. For in the intense field of the thundercloud, the electron which has already kinetic energy corresponding to a comparatively few kilovolts, and is moving anywhere nearly in the direction along which the field would carry it, will lose, by collisions, much less energy than it receives from the field. In consequence, it will continually increase in energy, while the chance of its being stopped by accidents of any kind becomes less and less as its energy increases. It is not impossible that in this way an electron may acquire energy corresponding to nearly the whole electromotive force of the thundercloud. Thus energies approaching, or even exceeding, that emitted as radiation on the destruction of a proton (10^9 volts) might be attained. Such ultra β-particles would have ranges comparable with the whole thickness of the atmosphere.

There is thus a possibility that ultra β particles from the region of maximum negative potential in the thundercloud may sometimes reach the upper atmosphere with a large part of their energy unexpended. Any such electrons will describe helical paths of large radius around the magnetic lines of force, and finally enter the lower atmosphere at widely separated parts of the earth. It is evident that these ultra β-particles would not be intercepted by mountains surrounding the place of observation. Millikan's experiments, made under these conditions, do not then rule out the possibility that thunderclouds may contribute to the penetrating ionising radiations which are generally regarded as being entirely of cosmical origin.

Hulburt * has examined this suggestion of Wilson, using the same equations which Epstein † employed in his work on high-speed electrons. He concludes that Wilson's hypothesis would lead to a penetrating radiation which is most intense at low latitudes, becoming feeble near the poles. This disagrees with Millikan's observations of the constancy of the cosmic radiation with latitude.

* *Phys. Rev.*, 37, 1 (1931).
† *Proc. Nat. Acad. Sci.*, 16, 658 (1930).

5. Lightning. Simpson * has investigated the phenomena of lightning, and has introduced some new ideas, which probably will have to be modified. For example, he says that the resistivity of the lower atmosphere in clear weather is approximately $4{\cdot}5 \times 10^{15}$ ohms. The values found for ebonite and sulphur are much greater than this, and good paraffin has a volume resistivity greater than 5×10^{18}. Simpson also considers that during a thunderstorm we have non-conducting clouds floating within a conducting atmosphere, thus completely reversing our ordinary ideas. It is difficult to believe that a cloud is a perfect non-conductor.

Simpson found that when a drop of water is broken up in the air without striking anything, a separation of positive and negative electricities takes place. The limiting velocity of a large raindrop falling vertically is about 8 metres per second. A drop larger than about 0·5 cm. in diameter is unstable ; it becomes flattened out and quickly breaks up into a number of small drops. When it breaks up it receives a positive charge. Now it is known that some of the air inside a thundercloud is moving with a vertical velocity, greater than 8 metres per second. The resulting negative charge is given to the air, and is absorbed by the cloud particles which are being carried upwards, We should expect, therefore, that the rain which falls where the air currents are vertical would be positively charged, and that at a distance from this region it would be negatively charged. This is in accordance with observation. There will be occasional discharges from the earth to the negatively charged cloud, but the most frequent discharges will be downwards towards the ground, some of them apparently ending in the air.

6. The Conduction of Electricity through Solutions. Molecules of acids, salts and bases, dissolved in solvents, are spontaneously ionised, the fraction of the dissolved molecules which are ionised being a function of the concentration of the solution. The un-ionised molecules do not contribute to the current through the solution, and other things being equal, a solution will have a smaller resistance, the greater the fraction of ionised molecules present in the solution. The specific conductivity per gram-equivalent per cubic centimetre, or, as it is termed, the *equivalent conductivity*, Λ, is given by * :

---

* *Nature*, **124**, 801 (1929).

$$= \frac{}{\nu N} = \alpha(u_K \quad u_A)F \tag{1}$$

where σ is the specific conductivity of the solution, N, the number of gram-molecules of solute per cubic centimetre of solution, ν, the valency of each ion into which each molecule is capable of ionising, F, the electrical charge associated with each gram-equivalent ion, known as the faraday and equal to 96,491 coulombs, α, the fraction of the molecules ionised, and u_A and u_K, the steady velocities in centimetres per second of the anion and kation, respectively, developed under unit potential gradient, 1 volt per cm.

While in general the specific conductivity decreases as the solution is diluted, the equivalent conductivity increases, tending towards a final limit, Λ_0, at infinitely great dilution. Hence, $d\Lambda/dN$ is negative, and formerly this fact was attributed almost entirely to $d\alpha/dN$ being negative, *i.e.*, the degree of ionisation increases as the solution becomes more and more dilute, approaching the value unity as N tends to zero, but actually only reaching this value when N is equal to zero. Debye and Hückel,† however, introduced a new theory which postulates that the molecules of a solute are completely ionised in dilute solutions even before infinite dilution is reached, the maximum concentration at which ionisation is complete depending upon the character of the solvent and solute. In badly-conducting solutions, *i.e.*, solutions of the so-called weak electrolytes, complete ionisation is never reached, while electrolytes of comparatively high conductivity, the so-called strong electrolytes, such as the uni-univalent salts, may be considered to be completely ionised even at concentrations greater than 10^{-4} normal.

7. Solvation of the Ions. Since electric forces polarise molecules, it is evident that the ions will polarise the molecules of a solvent in which they are situated, and any particular ion will be surrounded by oriented, polarised, solvent molecules held, more or less firmly to an extent which depends upon their distance from the ion. Hence, when the latter moves, under the influence of an external electric field, we should expect the ion to carry with it a sphere, or sheath, of the solvent. This effect is known as *solvation* of the ions. In the case of an anion in an aqueous solution the water molecules will be oriented with the hydrogen inwards, while those around the kation will be oriented with the oxygen inwards. The oriented molecules are strongly attracted to the central ion, and will tend to squeeze out any non-polar molecules from its immediate neighbourhood. This effect is known as the *salting-out process*.

---

* See Newman, " Electrolytic Conduction," p. 36 (1930).

† *Phys. Zeits.*, 24, 185, 305 (1923).

Now Stokes has shown that the retarding force acting on a sphere of radius b, when it moves through a fluid, is $6\pi b\eta u$ where η is the coefficient of viscosity of the fluid and u, the velocity of the sphere. Owing to solvation of the ions, it is evident that the radius b of an ion, as determined with the aid of Stokes's law, is greater than the radius b_0 of the ion proper, and the space occupied by the solvation envelope may be obtained by deducting the molecular volume of the ionic body proper from the ionic volume, as calculated by means of Stokes's law. If this result is divided by the molecular volume of a solvent molecule, the actual number of solvent molecules within the envelope is determined. It should be noted, however, that owing to the strong ionic forces existing within the solution, the packing of the molecules in the envelope will be much denser than in the free solvent. Ulich * has calculated some solvation numbers in this manner. His results are shown in Table XII., p. 342.

The solvation of the kations appears to be fairly constant for all solvents, whilst that of the anions is decidedly smaller in acetone, furfural and pyridine, than in the alcohols. The iodide ion seems to have a very small, if any, fixed solvation envelope in these solvents.

If we consider a simple case of conductivity, where the ions are deposited upon the electrodes during the passage of an electric current, $u_K/(u_K + u_A)$ will be the fraction of the electric charge

---

* *Trans. Farad. Soc.*, **23**, 392 (1927).

TABLE XII. SOLVATION NUMBERS.

Solvent.	Solvation Number.					
	Li^+.	Na^+.	K^+.	Cl^-.	Br^-.	I^-.
Water	6–7	2–4	—	—	—	—
Methyl alcohol	7	5–6	4	4	2–4	0–3
Ethyl alcohol	6	4–5	3–4	4–5	4	2–3
Acetone	4	4–5	4	2	1	0–1
Acetonitrile	—	5	3–4	—	1–3	0–2
Furfural	—	5	4	—	—	0–1
Pyridine	—	4	2–3	—	—	0–1

carried by the kations, and $u_A/(u_K + u_A)$ that conveyed by the anions. These ratios, which Hittorf termed *transference numbers* of the kation and anion, respectively, are denoted by the symbols n_K and n_A. Their values may be determined experimentally by various methods. Now, owing to solvation of the ions, it is evident that there will be a transport of solvent from one part of the solution to another, as the ions travel through the solvent. If $\mathbf{N}_s^A$ $\mathbf{N}_s^K$ represent the number of gram-molecules of solvent associated with each gram-anion and gram-kation, respectively, and $\mathbf{n}_A$, $\mathbf{n}_K$, the transference numbers in the absence of solvation, then the net electrolytic transference $\mathbf{N}_s$ of the solvent per faraday is given by :

$$\mathbf{N}_s = \mathbf{n}_K\mathbf{N}_s^K - \mathbf{n}_A\mathbf{N}_s^A \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

Various investigators * have shown that organic ions in water, at any rate the larger ions, do not carry water envelopes, so that it should be possible to determine the absolute value of the water carried by an inorganic ion in cases where the other ion is organic, since one of the terms of the right-hand side of equation (2) vanishes. Thus Remy and Reisener † found that if the electrolyte contained an organic kation, the direction of water transport was, in normal solutions, in the opposite direction to that of the electric current. In other words, the organic ion carried little, if any, water. These experimenters measured the water transport of aniline hydrochloride, and the value obtained represents the water carried by the chloride ion. Knowing the true transference numbers of this salt, they calculated N_s^A, the number of water molecules in the envelope surrounding the chloride ion, to be three. From this value they then determined the degree of solvation of other inorganic ions. Measurements were made, using chlorides, bromides and iodides, the hydration numbers of the chloride, bromide and iodide ions being 3, 2·1 and 3·7, respectively. From the results, shown below, it will be seen that there is fair agreement between the values as determined from the three solutions. The numbers quoted refer to the number of water molecules carried by each ion in normal solutions :

---

* Hevesy, *Jahrl. f. Radioakt und Elektromek.*, **11**, 419 (1914); **13**, 271 (1916). Lorenz, *Zeits. anorg. Chem.*, **94**, 240 (1916).

† *Zeits. phys. Chem.*, **126**, 161 (1927).

Ion.	Number of Water Molecules carried with each Ion in Solution.		
	Chlorides.	Bromides.	Iodides.
H^+	0·9	1·1	—
Li^+	12·6	—	—
Na^+	7·4	8·8	—
K^+	4·1	4·0	—
Cs^+	3·8	—	—
NH_4^+	4·4	—	—
NH_3OH^+	2·8	—	—
Mg^{++}	14·1	11·9	11·7
Ca^{++}	12·1	8·1	8·7
Sr^{++}	7·7	7·7	9·5
Ba^{++}	4·5	3·1	(7·8)

It will be noted that if the alkali metal kations are arranged in order of diminishing hydration, the cæsium atom occupies the lowest position.

8. Dimensions of Ions. Assuming that at infinite dilution the motion of an ion through a solvent obeys Stokes's law, the radius, *b*, of an ion can be calculated from the equation :

Force

where the force refers to that acting upon unit charge—$1{\cdot}59 \times 10^{-20}$ electromagnetic units—due to unit potential gradient, 1 volt per cm. $= 10^8$ electromagnetic units, η is the coefficient of viscosity of the solvent, and u, the velocity in cms. per second, developed under this potential gradient. If instead of u we use the mobility U, where $U = uF$, F being the faraday, then

$$b = \frac{8{\cdot}15 \times 10^{-9}}{\eta U} \text{ cm.} \tag{3}$$

It is important to note that the radius calculated is that of the ion and its associated solvent molecules, *i.e.*, those molecules which behave as if rigidly attached to the ion, and which move with it. Hartley and Raikes * have determined the radii of ions, both in water and in methyl alcohol, from their mobilities at 25° C., by means of equation (3). Their results, together with the effective ionic radii in the crystal lattice, are given in Table XIII.

TABLE XIII. IONIC RADIUS (ÅNGSTROM UNITS).

Ion.	In Water.	In Methyl Alcohol.	Crystal Lattice.	Ion.	In Water.	In Methyl Alcohol.	Crystal Lattice.
Li^+	2·30	3·78	0·72	$\frac{1}{2}Sr^{++}$	3·04	5·06	1·20
Na^+	1·79	3·27	1·01	$\frac{1}{2}Ba^{++}$	2·83	4·93	1·40
K^+	1·22	2·78	1·30	$\frac{1}{2}Zn^{++}$	3·36	5·02	0·60
Rb^+	1·17	2·60	1·50	$\frac{1}{2}Cd^{++}$	3·38	5·21	0·98
Cs^+	1·17	2·40	1·75	F^-	1·67	3·72	1·33
Ag^+	1·44	2·86	1·03	Cl^-	1·21	2·91	1·72
$\frac{1}{2}Mg^{++}$	1·44	5·19	0·75	Br^-	1·18	2·69	1·92
$\frac{1}{2}Ca^{++}$	3·05	4·98	1·02	I^-	1·20	2·45	2·19

The ions of the alkali metals and of the halogens, which have the largest radii in the crystal lattice, also have the highest mobilities, while all the ions of the divalent metals possess, approximately, the same mobilities, in spite of a considerable increase in size with atomic number. This is usually explained by assuming that the ions are solvated, and that the degree of solvation of the small ions is greater on account of the more intense electric field around them, their mobilities being correspondingly reduced.

---

* *Trans. Farad. Soc.*, **23**, 393 (1927).

As pointed out by Hartley and Raikes, the radii of all ions in methyl alcohol are greater than in water, the increase in apparent size being due, presumably, either to the larger solvent molecules, or to the greater number attached to the ion, the increase being more marked for the univalent than for the divalent ions. The influence of the ionic charge on the degree of solvation is shown by the fact that, in both solvents, all the divalent ions have the largest radii, although the radii in the crystal lattice vary. The silver ion, which is smaller than the rubidium and cæsium ions in the lattice, has a lower mobility in both solvents, while the thallium ion, which is larger than the silver ion in the lattice, moves more quickly than the latter, having, approximately, the same mobility as that of the rubidium and cæsium ions.

9. Theories of Electrolytic Conduction. There are two aspects to the problem of electrolytic conduction, namely, the well-defined equilibria which exist in solutions, and the mechanism whereby the conduction process is effected. As regards the equilibria, we apply the principles governing them, and support them by various assumptions, which involve an equation of state of the system. On the other hand, a theory of the conduction process demands a precise knowledge of the forces that occur between the charged particles and their surroundings. If we assume a force function, statistical methods can be employed in any investigation, and these statistical methods are now being developed and applied to electrolytic systems.

Many theories have been proposed to represent the actual nature of electrolytic solutions, some of which do account for the properties of one type of electrolyte, such as a weak one, but fail when applied to strong electrolytes. For example, Ostwald's dilution law is satisfactory when applied to weak organic acids, but strong acids and bases and their salts give results which are widely divergent from the theory.

Milner * assumed complete ionisation of electrolytes in dilute aqueous solutions, and taking into account the interionic forces, obtained an expression for the depression of the freezing point temperature, which agreed well with experimental results. The theory was also developed so as to apply to the electrical conductivity of electrolytic solutions.

---

* *Phil. Mag.*, **23**, 551 (1912) ; **25**, 742 (1913).

Debye and Hückel * deduced a relationship between the equivalent conductivity and the concentration, which is based on two general principles, one the so-called *Boltzmann's principle* from the kinetic theory of gases, and the other, known as *Poisson's equation*, is derived from the law of electrostatics, and involves Coulomb's law. They applied these principles, in the first place, to determine the distribution of the ions of opposite charges around any selected ion, and to evaluate the potential that prevails around the ion in consequence of its own charge and of the unequal distribution which it produces in the surrounding ions.

Consider an ion having an electrical charge equal to e. This ion produces in any shell of volume $\delta \mathrm{v}$, located between distances r and $r + \delta r$, a potential, ψ, and a density of electric charge ρ. Now, if a large number of molecules possess an average kinetic energy, $\frac{3}{2} kT$, and are distributed throughout a region in which exist, at different points, different fields of force, there will be, accordingly, different potentials, and any kind of molecule, in a volume $\delta \mathrm{v}$, will acquire a definite potential energy, E. The number of molecules in this volume which possess energy E, will equal the number of molecules per unit volume, at a place where E is zero, multiplied by the factor $\epsilon^{-E/kT}$ and the volume $\delta \mathrm{v}$, where ϵ is the base. of Naperian logarithms. This result is known as Boltzmann's principle, and k is Boltzmann's constant.

Consider an ion migrating in a solution, and imagine a line of fixed length connected with the ion in such a way that during the migration of the ion, the direction of this line in space is maintained constant. At the end of the line we imagine an elementary volume. If we consider the ion and its elementary volume for a certain time, we find that sometimes an excess of positive, and sometimes an excess of negative, electrical charge is contained within the elementary volume, due to the various ions within the solution. Taking the time integral of this charge, and dividing by the whole time of observation, we obtain the mean charge within the element. The density of the electricity within the space surrounding an ion—this space is known as the *ionic atmosphere*—is thus the mean charge divided by the volume, and it is obvious that, so far as the Coulomb forces alone are considered, the electrical density within the ionic atmosphere will be of opposite sign to the charge on the ion. Thus, the ionic atmosphere surrounding any selected positive ion will contain an excess of negative electricity. This will cause an average electrical potential ψ, and an average electrical density ρ, to exist at any distance from the selected ion. If we apply Boltzmann's distribution principle, we have :

---

* *Phys. Zeits.*, **24**, 185 (1923).

$$\rho = ne\,(\epsilon^{-e\psi/kT} - \epsilon^{e\psi/kT}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where e is the charge on a positive ion, T, the absolute temperature, and n, the number of positive ions per c.c. of solution.

Assuming Poisson's equation,

$$\nabla^2\psi = -\frac{4\pi\rho}{K}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where K is the dielectric constant of the medium in which the ions are situated, we have from equations (4) and (5),

$$\nabla^2\psi = -\frac{4\pi en}{K}(\epsilon^{-e\psi/kT} - \epsilon^{e\psi/kT}),$$

or,

$$\nabla^2\psi = \frac{8\pi en}{K}\sinh\frac{e\psi}{kT}.$$

The average potential in the space around the selected ion depends only upon the distance from the ion, and for small values of the potential, ψ, we may write

$$\sinh\frac{e\psi}{kT} = \frac{e\psi}{kT},$$

and thus,

$$\nabla^2\psi = \frac{8\pi e^2 n\psi}{KkT}.$$

Transforming to polar co-ordinates

$$\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial\psi}{\partial r} = \kappa^2\psi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $$\kappa^2 = \frac{8\pi e^2 n}{KkT},$$

$\frac{1}{\kappa}$ having the dimension of a length, and being known as the *thickness of the ionic atmosphere.* It is a characteristic factor in the theory of Debye and Hückel.

Integrating equation (6) we obtain,

$$\psi = \frac{A\epsilon^{-\kappa r}}{r},$$

where A is a constant, so that if r is small, *i.e.*, if we consider points not far removed from the ion,

$$\psi = \frac{A}{r} - A\kappa,$$

and this expression represents the total potential at a point distant r from an ion. But this potential is made up of two parts, namely, that due to the ion, if there were no surrounding ions, and that arising from the ionic atmosphere, *i.e.*, from the unequal distribution of the positive and negative ions in the surroundings. At infinite dilution, the potential at a point will be that due to the ion alone, e/Kr, so that $A = e/K$, and thus the potential at points very close to the ion, arising from the existence of the ionic atmosphere, is given by :

$$\psi = -A\kappa = -e\kappa/K.$$

In other words, the potential of the ion itself, resulting from the ionic atmosphere is $-e\kappa/K$.

If the electrolyte is not a simple one, then,

$$\kappa^2 = \frac{4\pi}{KkT}\sum n_i e_i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

n_i being the number of the ions of the ith sort.

Debye and Hückel assumed that strong electrolytes in dilute solutions are completely ionised, and they attributed the variations of the conductivity with concentration to changes in the ionic mobilities, and not to any change in the fraction of the number of molecules ionised. The velocity of an ion, as it moves through a liquid, depends upon the accelerating forces produced by electrical forces and the frictional, or retarding, forces which always act upon a body moving through a viscous medium.

An ion at rest possesses a symmetrical ionic atmosphere, but the symmetry will be destroyed as soon as the ion moves. Thus, when an external electric field is applied to an electrolytic solution, an ion moves, say, to the right, and during its motion it will have to build up, as it were, an electrical charge density to the right, but to the left of the ion the electrical charge density is too large, and will have to decrease. If the ionic atmosphere were created, or changed in value, instantaneously, the central symmetry would exist, even during the ionic motion, but this is not the case. Since the charge density in the ionic atmosphere is always opposite in sign to that of the charge on the ion, it follows that the ion will be subjected to an electric force, due to this lack of symmetry, and the direction of this force will be opposed to that exerted by the external electric force. Debye and Hückel showed that the value of this opposing electric force is equal to :

$$-\frac{e_i \kappa \zeta}{6KkT} u_i,$$

where

$$\zeta = \frac{\sum n_i e_i^2 \zeta_i}{\sum n_i e_i^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

n_i is the number of ions of the ith kind per c.c., e_i the charge on the ion of this kind, u_i its velocity, and ζ_i a friction coefficient, such that when multiplied by the mean velocity of the ion, the result is equal to the frictional force, due to the viscosity of the medium, which the ion has to overcome during its steady motion. Thus we have two electric forces acting in opposite directions upon any one ion.

For steady ionic motion, these two forces are in equilibrium with any opposing frictional forces which may act upon the ion, as it moves through the liquid. For infinitely dilute solutions, there will be only one such retarding force, namely, that which is always exerted upon a body when it moves through a medium possessing viscosity. The value of this force is, by Stokes's law,

$$6\pi b_i \eta u_i \text{ or } \zeta_i u_i,$$

where b_i is the radius of the ion, and η, the coefficient of viscosity of the liquid. But if the solution is not infinitely dilute, the charge on the ionic atmosphere will also be acted upon by the external electric force, and, accordingly, since the sign of this charge is opposite to that upon the ion, there will be created an additional relative motion between the ion and its atmosphere, and thus an extra force, tending to oppose the motion of the ion through the fluid. This will have the effect of increasing the apparent frictional force by an amount,

$$e_i X b_i \kappa,$$

where X is the external electric force. Thus, the total retarding viscous force, opposing the motion of the ion through the liquid is equal to :

$$\zeta_i u_i + e_i X b_i \kappa.$$

For steady ionic motion through the solvent, the sum of the accelerating electrical forces, acting upon an ion, must be equal to the total frictional or retarding forces, and thus,

$$e_i X - \frac{e_i^2 \kappa \zeta u_i}{6KkT} = \zeta_i u_i + e_i X b_i \kappa,$$

or,

$$u_i = \frac{e_i X}{\zeta_i} \cdot \frac{1 - b_i \kappa}{1 + \dfrac{\zeta}{\zeta_i} \cdot \dfrac{e_i^2 \kappa}{6KkT}},$$

i.e.,

$$u_i = \frac{e_i X}{\zeta_i}\left[1 - b_i \kappa - \frac{\zeta}{\zeta_i} \cdot \frac{e_i^2 \kappa}{6KkT}\right], \text{ approximately} \quad . \quad (9)$$

At infinite dilution $\kappa = 0$, and,

$$(u_i)_0 = \frac{e_i X}{\zeta_i}.$$

Since the equivalent conductivity, Λ, is proportional to the ionic velocity, we see that the change in Λ, produced by changes in the concentration, is proportional to κ. But κ, the reciprocal of the radius of the ionic atmosphere, is proportional to the square root of the concentration, equation (7), and therefore this theory of interionic attraction leads to Kohlrausch's formula for the relation between equivalent conductivity and concentration.

Now the specific conductivity, σ, of an electrolytic solution is equal to :

$$\frac{1}{X}\sum n_i e_i u_i,$$

and so from equation (9),

$$\sigma = \sum \frac{n_i e_i^2}{\zeta_i} - \left[\sum \frac{n_i e_i^2 b_i}{\zeta_i} + \sum \frac{n_i e_i^4}{6KkT} \cdot \frac{\zeta}{\zeta_i^2}\right]\kappa.$$

At infinite dilution,

$$\sigma_0 = \sum \frac{n_i e_i^2}{\zeta_i}.$$

Thus, using the values of ζ and κ, as given in equations (8) and (7), respectively, we have :

$$\frac{\sigma_0 - \sigma}{\sigma_0} = \sqrt{\frac{4\pi}{KkT}\sum n_i e_i^2}\left[\frac{\sum \frac{n_i e_i^2 b_i}{\zeta_i}}{\sum \frac{n_i e_i^2}{\zeta_i}} + \frac{\sum n_i e_i^2 \zeta_i}{\sum n_i e_i^2} \cdot \frac{\sum \frac{n_i e_i^4}{6KkT\,\zeta_i^2}}{\sum \frac{n_i e_i^2}{\zeta_i}}\right].$$

Suppose that every molecule of solute, when in solution, ionises into z_1, z_2, *etc.*, ions of valencies ν_1, ν_2, *etc.*, then,

$$\frac{\sigma_0 - \sigma}{\sigma_0} = \sqrt{\frac{4\pi e_0^2}{KkT} \cdot zn}\left[b w_2 + \frac{e_0^2}{6KkT} w_1\right], \quad . \quad . \quad (10)$$

where $\pm e_0$ is the charge on a univalent ion, n, the number of molecules of solute per c.c., and

$$z = \sum z_1,\ z_2,\ etc.,$$

$$w_1 = \frac{\sum z_1 \nu_1{}^2 \zeta_1}{\sqrt{z \sum z_1 \nu_1{}^2}} \cdot \frac{\sum \dfrac{z_1 \nu_1{}^4}{\zeta_1{}^2}}{\sum \dfrac{z_1 \nu_1{}^2}{\zeta_1}},$$

$$w_2 = \sqrt{\frac{\sum z_1 \nu_1{}^2}{z}},$$

and

$$b = \frac{\sum \dfrac{z_1 \nu_1{}^2 b_1}{\zeta_1}}{\sum \dfrac{z_1 \nu_1{}^2}{\zeta_1}}.$$

For example, in the case of a uni-univalent electrolyte, such as potassium chloride, $z_1 = z_2 = 1$ and $\nu_1 = \nu_2 = 1$, so that,

$$w_1 = \frac{\zeta_1 + \zeta_2}{2} \cdot \frac{\dfrac{1}{\zeta_1{}^2} + \dfrac{1}{\zeta_2{}^2}}{\dfrac{1}{\zeta_1} + \dfrac{1}{\zeta_2}} = \frac{\zeta_1{}^2 + \zeta_2{}^2}{2\zeta_1\zeta_2},$$

$$w_2 = \sqrt{1} = 1,$$

and

$$b = \frac{\dfrac{b_1}{\zeta_1} + \dfrac{b_2}{\zeta_2}}{\dfrac{1}{\zeta_1} + \dfrac{1}{\zeta_2}} = \frac{b_1\zeta_2 + b_2\zeta_1}{\zeta_1 + \zeta_2}.$$

Now the equivalent conductivity, Λ, is given by $\Lambda = 1{,}000\ \sigma/C$, where C is the concentration in gram-molecules per litre, and $n = NC/1{,}000$, N being the number of molecules per gram-molecule. Hence for aqueous solutions of uni-univalent electrolytes at 18° C., we have, on substituting the values of the various constants in equation (10),

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = \left[0{\cdot}233 \times 10^8 \frac{b_1\zeta_2 + b_2\zeta_1}{\zeta_1 + \zeta_2} + 0{\cdot}273 \frac{\zeta_1{}^2 + \zeta_2{}^2}{2\zeta_1\zeta_2}\right]\sqrt{2C},$$

and we thus obtain the relation between the equivalent conductivity and the concentration of an electrolyte, as found empirically by Kohlrausch.

Debye and Hückel have made a comprehensive survey of conductivity data for dilute aqueous solutions, and have shown that they are in fair agreement with their theory. Similar comparisons for non-aqueous solvents are more difficult, as the experimental data are far less homogeneous and complete, but Hartley and Frazer [*] have shown that the relationship between equivalent conductivity and concentration does hold for many uni-univalent salts in methyl alcohol up to 0·002 normal. Hartley [†] has measured the conductivity of KI in different solvents. For water and for methyl alcohol, the calculated slope of the Λ/Λ_0 curve is greater than the observed slope, but for ethyl alcohol and acetone the agreement is very close. Other salts give better agreement in some solvents than in others. Many other investigators have verified experimentally the conductivity values as calculated by means of Debye and Hückel's theory.[‡]

There is a considerable mass of experimental evidence, however, which indicates that the theory must be modified in many cases. Even in dilute salt solutions, specific chemical interaction between the ions may be of importance, as well as the normal electrical attraction which exists between them. Bjerrum [§] has concluded that in certain electrolytes a proportion of the ions will form pairs, which will act osmotically as single molecules if one or both of the ions has a radius smaller than a critical value. MacInnes and Cowperthwaite's computations [||] favour Bjerrum's conclusions, although the latter call for larger degrees of association than those found by the former experimenters. McBain and Rysselberge's results[¶] for complex ions indicate that the real value of α, the degree of ionisation, must be less than unity. Other evidence against complete ionisation in all dilute electrolytes has been brought forward by Nernst [*] Fajans,[†] Jacobs and King,[‡] and others.

---

[*] *Proc. Roy. Soc., A*, **109**, 351 (1925).

[†] *Nature*, **119**, 322 (1927).

[‡] See *Trans. Farad. Soc.*, **23**, 333 (1927).

[§] *Kgl. Danske Viden. Sels.*, **7**, 9, 2 (1926).

[||] *Trans. Farad. Soc.*, **23**, 400 (1927).

Journ. Amer. Chem. Soc., **50**, 3009 (1928) ; **52**, 2336 (1930).

Rabinowitsch,[§] criticising the theory of complete ionisation, suggests that the mechanism of conduction in solutions is of two kinds: transference of charge by means of ionic migration through the solution (predominating in dilute solutions) and change in position of the ions in the interior of a complex molecular aggregate, analogous to ionic conductivity in crystals, this occurring mainly in concentrated solutions.

Onsager [‖] has modified Debye and Hückel's theory, taking into account the Brownian motion of the ions which has an effect on the dissymmetry of the ionic atmosphere.

10. The Dielectric Constant of Electrolytic Solutions. The dielectric constant of an electrolytic solution plays an important part in modern electrolytic theories. Walden [¶] has shown that the value of this constant for a solution is less than that for the pure solvent. Now at molecular distances from the ions, we have to deal with very large electrical fields of the order of 10^6 volts per centimetre, and thus the ions set up electrical saturation in the neighbouring molecules of a solvent, such as water. If, furthermore, we consider only very dilute solutions, it will not be necessary to take into account the mutual interaction between the ions. Within the neighbourhood of the ions, then, the solvent molecules will assume positions with their moments parallel to the radial field.

When a small measuring field is applied between two parallel planes in the electrolytic solution, since the field due to the ions will have oriented the neighbouring solvent molecules, the small measuring field cannot orient them as much as it does in the pure solvent, and thus we may look upon the saturation effect, produced by the ions, as the equivalent of making holes, as it were, in the solvent around each ion, the radii of the holes depending upon the distance to which the saturation effect extends.

---

[*] *Zeits. Elektroc.*, **33**, 428 (1927).
[†] *Trans. Farad. Soc.*, **23**, 357 (1927).
[‡] *Journ. Phys. Chem.*, **34**, 1013 (1930); **35**, 480 (1931).
[§] *Zeits. phys. Chem.*, **147**, 345 (1930).
[‖] *Phys. Zeits.*, **27**, 388 (1926); **28**, 277 (1927).
[¶] *Zeits. phys. Chem.*, **110**, 44 (1924); **116**, 261 (1925).

From these considerations we should expect the specific inductive capacity of a salt solution to be less than that of the pure solvent. This expectation is realised in practice. Thus Sack [*] has shown that for very dilute solutions, the dielectric constant decreases linearly as the concentration is increased. He used solutions of salts of various types, including potassium chloride, barium chloride, and copper sulphate. The ions formed from these salts carry different charges, and this fact was found to affect the dielectric behaviour of the electrolyte. His results show that:

$$K = K_0(1 - \mathbf{b}C),$$

where K is the specific inductive capacity of the solution, K_0, that of the pure solvent, C, the concentration, and **b**, a constant which is characteristic of the kind of ions.

Now Sack recognised that if the effect is a saturation one, the value of **b** should depend only upon the charge on the ions, and not upon other physical characteristics, at least to a first approximation. He found that the value of **b** could be determined by a summation process extended over all the different kinds of ions, and that for a single ion, its value should be proportional to $\nu^{\frac{3}{2}}$, where ν is the valency of the ion. He verified this conclusion from his experiments on different salts.

The specific inductive capacity of a large number of solutions has been measured by Walden, Ulich and Werner.[†] In all cases they found a lowering of the dielectric constant, proportional to the concentration at low concentrations, but there was a minimum value beyond which the dielectric constant increased with concentration. Walden and Werner,[‡] Hellmann and Zahn,[§] Nayder,[||] Partington and Rule [¶] and many others have investigated this effect, and the reader is advised to consult the paper by Blüh [**] for a full description of recent work on dielectric constants. For example, Hellmann and Zahn found that electrolytes were

[*] *Phys. Zeits.*, **27**, 206 (1926); **28**, 199 (1927).

[†] *Zeits. phys. Chem.*, **116**, 261 (1925).

[‡] *Ibid.*, **124**, 405 (1926).

[§] *Phys. Zeits.*, **27**, 636 (1926).

[||] *Acad. Pol. Sci., et Lettres Bull.*, No. **7**, (a), 247 (1925).

[¶] *Phil. Mag.*, **1**, 1035 (1926).

[**] *Phys. Zeits.*, **27**, 226 (1926).

divisible into two groups : those, such as hydrochloric acid, which even at high concentrations show little lowering of the dielectric constant, and those, like copper sulphate, which show the effect even at very low concentrations.

The variation of the specific inductive capacity, with changing salt concentration, makes the self potential of the ion, which was neglected in the original Debye and Hückel theory for the case of dilute solutions, appear as a significant factor in the domain of concentrated solutions.*

In solvent media which possess smaller specific inductive capacities than that of water, the increased interionic forces will cause larger deviations from the ideal laws of solution. We must expect the limit of the application of Debye and Hückel's theory, for such solutions, to be at a still lower concentration than for aqueous solutions. The tendency of ions to associate, which, of course, increases with increasing electrical charge and with decreasing ionic size, will be more marked for such solvents. Substances which are practically strong electrolytes in water may prove to be weak, or incompletely, dissociating substances in non-aqueous solvents.

11. The Wien Effect. In general, the electrical conductivity of a solution is independent of the applied potential difference, but Wien,† using voltages up to 80 kilovolts per cm., found that in certain solutions the equivalent conductivity increased with the applied electric force. This potential effect, or *Wien effect,* as it is called, increases rapidly with the valency of the ions. At first the conductivity increases linearly, approximately, with the field strength. With very strong fields, however, it tends to a constant value—the limiting value. The initial rise of conductivity is greater, the more dilute the solution. In very dilute solutions the limiting value is attained with comparatively small field values.

Wien found that the change in conductivity, $\delta\Lambda$, produced by an electric force, X, could be represented by the formula :

$$\delta\Lambda = AX^2(1 - BX^2),$$

---

* See Hückel, *Phys. Zeits.*, **26**, 93 (1925).

† *Ann. d. Phys.*, **83**, 327 (1927) ; **85**, 795 (1928). See also Jones and Bollinger, *Journ. Amer. Chem. Soc.*, **53**, 1207 (1931).

where A is proportional to the square of the product of the valency of the ions, inversely proportional to the square root of the concentration, and depends to a certain extent upon the nature of the ions. The value of B likewise increases with the product of the valencies, and decreases with the concentration.

Joos and Blumentritt * suggested the formula :

$$\delta\Lambda = AX^2 - BX^4 + CX^6 \ldots,$$

for very strong fields.

The probable explanation of the effect is that it arises from a mutual slowing up of the ions, arising from the presence of the ionic atmosphere. The asymmetrical electrical charge distribution in the ionic atmosphere gives rise to the *electrical force of relaxation*,† and when the force acting upon an ion is suddenly changed, it takes a finite time interval (time of relaxation) for equilibrium to be established. The values of the time of relaxation for various electrolytes at 10^{-3} normal and at 18° C. are given below. In addition, the wave-length, corresponding to electrical oscillations of periodic time equal to the times of relaxation, are included.

Electrolyte . . .	KCl	HCl	$MgCl_2$	$CdSO_4$	$LaCl_3$
Time of relaxation $\times 10^7$ sec.	0·553	0·189	0·323	0·314	0·208
Corresponding wave-length (metres) . . .	16·6	5·67	9·69	9·44	6·24

When the applied electric fields are very intense, the resulting values of the ionic velocities are very high. In some of Wien's experiments they were of the order of 1 metre per second. Under these conditions the ions will travel over a distance many times greater than the thickness of the ionic atmosphere during the time of relaxation. The ionic atmospheres are not built up, and in such very strong fields the force of relaxation is of little, if any, consequence. Thus the equivalent conductivity under these conditions will approach the value at infinite dilution, and so, at any given concentration, the conductivity increases as the strength of the applied electric field is raised.

---

* *Phys. Zeits.*, **28**, 836 (1927).

† See Sections 1 and 9.

Bauer * found that for solutions in acetone the results were similar to those for aqueous solutions, but the constant A is greater, and B smaller, for acetone solutions.

12. Conduction Dispersion. The conductivity of an electrolytic solution also varies with the frequency of an applied alternating electric field. This effect is known as *conductivity dispersion*, and is due to the disappearance of the electrical force of relaxation, brought about by the high frequency of the applied electrical force.

Falkenhagen and Williams † expressed the molecular conductivity, λ, as a function of the frequency of the electrical force thus :

$$\lambda = \lambda_0 - \lambda_1 - \lambda_2,$$

where λ_0 is the molecular conductivity at infinite dilution, λ_1, the electrical force of relaxation, and λ_2, the ordinary force of electrophoresis, *i.e.*, the viscous force exerted on the ions due to the action of the applied electric force on the ionic atmosphere. Both λ_1 and λ_2 are expressed as molecular conductivities. The values of λ_0, λ_1 and λ_2 for different electrolytes, are given below, C, the concentration being expressed in gram-molecules per litre of solution. Concentration, mobility of ions, dielectric constant and temperature all influence conductivity dispersion.

Electrolyte.	Temperature °C.	λ_0	λ_1.	λ_2
KCl . .	18	130	$29{\cdot}1 \times \sqrt{C}$.	$50{\cdot}5 \times \sqrt{C}$.
HCl . .	18	380	85·2 ,,	50·5 ,,
$LiCl$ . .	18	98	22·0 ,,	50·5 ,,
$MgCl_2$ . .	18	222	150 ,,	262·4 ,,
$MgSO_4$ . .	18	229	410 ,,	404·0 ,,
$LaCl_3$ . .	18	345	524 ,,	743·0 ,,
$K_4Fe(CN)_6$.	25	680	1440 ,,	1890·0 ,,
$Ca_2Fe(CN)_6$.	25	620	3920 ,,	2485·0 ,,

---

* *Ann. d. Phys.* **6**, 253 (1930).

† *Journ. Phys. Chem.*, **33**, 1121 (1929).

The effect has also been investigated by Rieckhoff,[*] Brendel, Mittelstaedt and Sack [†] and by Deubner.[‡] The frequencies employed were round about 10^7 per second.

13. Superconductivity. Kamerlingh Onnes [§] found that, with mercury, instead of a continuous decrease of resistance with fall in temperature, there was a sudden disappearance of the resistance in the neighbourhood of the boiling-point temperature of liquid helium, 4·2° K. Within a temperature range of less than 0·02°, the resistivity dropped from a perfectly definite value (about 0·0005 of its value at 0° C.) to a value less than he could detect with a sensitive galvanometer, certainly less than 10^{-9} times its value at 0° C.

It was found later that other metals exhibit this property, tin at 3·8° K., lead at about 6° K., thallium at 2·47° K., indium at 3·41° gallium at 1·1° K., and tantalum at 4·2° K.[‖]

Recently, van Aubel, de Haas and Voogd [¶] have measured the resistance of compounds of two metals in which one of the components belonged to the superconducting metals. They examined rods of Cu_3Sb, Ag_3Sb, Ag_3Sn, Cu_3Sn, Bi_5Tl_3, and SbSn between 273° K. and 14° K. The resistance of Cu_3 Sb and Ag_3Sb varied slightly with temperature, decreasing less than that of their components. At temperatures in the neighbourhood of liquid helium, superconductivity was developed in the resistances of Bi_5Tl_3, SbSn, and Sb_2Sn_3. The rod of Bi_5Tl_3 became superconducting even above the boiling-point temperature of helium, although thallium only becomes superconducting at 2·47° K., and bismuth retains its full resistance down to 1·5° K. In the cases of SbSn and Sb_2Sn_3 the resistance began to fall rapidly at higher temperatures than with pure tin, 3·8° K. So that in all three substances superconductivity is more easily induced than in their superconducting components. This peculiarity is not, however, a general rule.

---

[*] *Ann. d. Phys.*, **2**, 577 (1929).

[†] *Phys. Zeits.*, **30**, 576 (1929), **32**, 327 (1931).

[‡] *Ibid.*, **30**, 946 (1929).

[§] *Comm. Phys. Lab. Leiden*, No. 120 ; No. 133.

[‖] *Ibid.*, Nos. 160, 167, 193 ; Meissner, *Naturwiss.*, **17**, 390 (1929) ; *Phys. Zeits.*, **29**, 897 (1928) ; McLennan, Howlett and Wilhelm, *Trans. Roy. Soc., Canada*, **23**, 287 (1929).

[¶] *Comm. Phys. Lab. Leiden*, No. 193.

McLennan, Allen and Wilhelm * made determinations of the superconducting temperatures of alloys containing either Bi or Sb, and from the results it was concluded that non-superconductors alloyed with superconductors do not appreciably affect the superconductivity.

Recently, Meissner and Fränz † have measured the superconductivity of some carbides and nitrides. Most show the effect, some of them at a temperature as high as 10° K.

The disappearance of the resistance of all superconductors, when measured with small current densities, takes place at a very definite temperature, but when very large current densities are used, the critical temperature is considerably lowered. It seems that for each current density there is a certain critical temperature, and for each temperature a certain *threshold current* below which the resistance vanishes. In some cases current densities as great as 900 amperes per square millimetre can be used without producing appreciable resistance.

Superconductivity is also disturbed by a magnetic field, the effect being determined by the temperature, and by the direction of the field with regard to the windings of the wire. Tuyn and Onnes ‡ investigated this effect on the superconductivity in the cases of lead, tin and indium. They found that these substances remained superconducting until a certain critical field strength, called the *magnetic threshold* value, was reached, and then suddenly showed a considerable resistance, which increased gradually with further increase in the field strength. Silsbee § suggested that the magnetic threshold value and the threshold current are directly connected by the relationship, that the latter is the value of the current at which the magnetic field, due to the current itself, is equal to the magnetic threshold value. The importance of this hypothesis is evident, as its correctness would account for the current threshold value. Experiments are in good agreement with the hypothesis. Tuyn and Onnes found the following relationship :

---

* *Roy. Soc. Canada, Trans.*, 24, 25, 53 (1930).

† *Zeits. f. Phys.*, 65, 30 (1930).

‡ *Comm. Phys. Lab. Leiden*, No. 174.

§ Bureau of Standards, *Scientific Papers*, No. 307 (1917).

$$H_{\frac{1}{2}} = h(T_s^2 - T^2),$$

where $H_{\frac{1}{2}}$ is the magnetic field which restores half of the resistance, measured at a temperature T, h, a constant and T_s, the vanishing-point temperature, the value of which varies with the metal. The measurements were made on micro-crystalline wires, in fields which were gradually increased in strength at constant temperature ; the direction of the magnetic field was transverse to that of the current.

Tuyn * has also investigated the effect of a magnetic field on the superconductivity of thallium. The method used was that of compensating the potential at the extremities of the known and unknown resistance, connected in series, by the aid of a special compensation apparatus. From the potential differences, he calculated resistances as if Ohm's law were valid below the threshold temperature. With the magnetic field transverse to the direction of the current, the following results were obtained :

Temperature K .	2·47°	2·21°	2·19°	1·85°	1·83°
$H_{\frac{1}{2}}$ (gauss) . .	0	31	34	65	67

With thallium, the transverse effect does not satisfy a quadratic relation as closely as in the case of tin. Deviations up to 5 per cent. are found between the observed values and those calculated from the equation :

$$H_{\frac{1}{2}} = -25{\cdot}4\,T^2 + 154{\cdot}9.$$

The constant h appears to be larger than for tin and indium.

It has been found that with the magnetic disturbance of the superconductivity of tin and mercury, hysteresis phenomena appear in the change of resistance. If the magnetic field strength is increased, the resistance value is regained at a higher field strength than that at which it disappeared in a decreasing magnetic field.† De Haas and Voogd ‡ found that this hysteresis phe-

---

* *Comm. Phys. Lab. Leiden*, No. 191.

† See Sizoo, de Haas and Onnes, *Comm. Phys. Lab. Leiden*, No. 180.

‡ *Ibid.*, No. 191.

nomenon appears in all superconducting metals. It seems to occur most markedly when there are large crystals, and when the magnetic field is homogeneous.

De Haas and Voogd * investigated the magnetic disturbance of the superconductivity of Bi_5Tl_3 and found that the value of $\mathrm{H}_{\frac{1}{2}}$ increases more rapidly with decreasing temperature than in the case of pure superconductors. This unexpected result may become of use in magnetic researches because of the high values of $H_{\frac{1}{2}}$ found for Bi_5Tl_3.

After the discovery of superconductivity the idea of *micro-residual resistance* was introduced. An upper limit of this was taken to be the quotient of the minimum perceptible potential difference and the current threshold value, assuming Ohm's law to be valid. In this way, with a small coil only 1 cm. long, containing 1,000 windings of lead wire, which remained superconductive even when 0·8 amp. was passed, it was found that:

$$\frac{\text{Resistance at } 1{\cdot}8^\circ \text{ K.}}{\text{Resistance at } 273^\circ \text{ K.}} = 0{\cdot}5 \times 10^{-10},$$

for lead at 1·8° K. According to Silsbee's hypothesis, the effect of the magnetic field of the current comes into play and gives an apparent micro-residual resistance, even if the real resistance of the superconductor were rigorously zero.

If the minimum perceptible potential is V, the threshold current i, and the limit of the apparent micro-residual resistance R, then:

$$V$$

and if we take i equal to the value obtained from $H = \frac{2i}{r}$, where H is the magnetic threshold value (due to a straight wire of radius r)

$$H = h_1(T_s^2 - T^2),$$

and then

$$R = \frac{2V}{rH} = \frac{2V}{h_1 r(T_s^2 - T^2)}.$$

Thus the relation for R is rather complicated, but the theory gives a qualitative explanation of the observed phenomena whereby the magnetic field of the threshold current produces an apparent micro-residual resistance.

---

* *Ibid.*, No. 199; see also No. 214.

Several explanations [*] of superconductivity have been advanced, but it cannot be said that any of them are entirely satisfactory. Kapitza [†] supposes that the main cause of the phenomenon lies in the mechanism which makes his additional resistance disappear. He supposes that this additional resistance is very similar to the one produced by a magnetic field, distributed at random in the metal, and it is natural to expect that the disappearance of the additional resistance is made more difficult when the field is large. This explains the influence of the magnetic field on the threshold temperature of superconductivity which, according to Kapitza's views, moves to lower temperatures in a magnetic field, this shift of the threshold temperature increasing as the magnetic field becomes stronger. From his experiments he found that a strain set up in the metal is equivalent to an increase in the disturbing internal magnetic field, and this again should move the threshold of superconductivity to lower temperatures. Such an effect was actually observed by Kamerlingh Onnes in tin and indium.

Kapitza suggests that by affecting the chemical and physical state of the metal, *e.g.*, by means of very careful crystallisation and by avoiding all possible strains, superconductivity may be produced in all metals.

Bartlett [‡] criticises this suggestion, and proposes a superconductivity model which gives a qualitative picture of most of the facts. The crystal is supposed to be composed of two systems, the lattice with its characteristic vibrations, and the electron system, considering the lattice ions at rest. These systems can be treated by wave mechanics, and it may be assumed that in the superconducting state the lattice has not sufficient energy to impart it in the form of kinetic energy to the electrons, but that the latter may change their magnetic energy. As a result, there is little or no electrical resistance. Kapitza [§] points out certain difficulties which arise in applying Bartlett's theory, which he considers a very interesting one, requiring to be worked out and tested by experiment. It does not account for the suddenness with which superconductivity appears. Meissner and Scheffers [*] also criticise Kapitza's theory of superconductivity.

---

[*] See Lindemann, *Phil. Mag.*, **29**, 127 (1915); Thomson, *ibid.*, **30**, 192 (1915).

[†] *Proc. Roy. Soc.*, *A*, **123**, 356 (1929). See also section 23, Chapter VII.

[‡] *Nature*, **123**, 869 (1929).

[§] *Ibid.*

Houston [†] has shown that electrical resistance is caused by the diffraction of electron waves, the irregular motion of the ions of the crystal lattice, due to temperature energy, causing a general scattering of the waves in all directions. Frenkel and Mirolubow,[‡] using the work of Brillouin [§] on the scattering of light, find that the resistance should increase with the third power of the temperature at very low temperatures.

All these treatments are based upon the idea that the resistance of a metal is due wholly to the temperature motion of the ions in the crystal lattice. Hence, if the resistance becomes zero at the absolute zero of temperature, it must be assumed that the temperature motion of the ions also becomes zero at this point. But it is almost certain that this is not the case. On the one hand, the quantum theory in its present form indicates that a harmonic oscillator in its lowest state possesses a half-unit of energy, *i.e.*, $E_0 = \frac{1}{2}h\nu$, and, therefore, presumably a considerable amount of motion. On the other hand, the experiments which have been made to determine the intensity of the X-ray diffraction pattern, as a function of the temperature, seem to point rather clearly to the existence of zero-point energy, and a zero-point motion of the system. [‖]

Houston [¶], too, has pointed out that it is necessary to take into account the restrictions placed upon the electron scattering by the quantum statistics. Then the Brillouin treatment of wave scattering gives a very satisfactory law of the temperature dependence of resistance, and explains the fact that the resistance of a pure metal becomes zero at the absolute zero of temperature.

---

[*] *Phys. Zeits.*, **30**, 827 (1929).
[†] *Phys. Rev.*, **34**, 279 (1929).
[‡] *Zeits. f. Phys.*, **49**, 885 (1928).
[§] *Ann. d. Phys.*, **17**, 88 (1922).
[‖] See James, Waller and Hartree, *Proc. Roy. Soc.*, *A*, **118**, 334 (1928).
[¶] *Loc. cit.*

No theory of electronic conductivity, so far advanced, seems to account adequately for the phenomenon of superconductivity; in fact, the greatest difficulty lies not so much in explaining the superconducting state, as in accounting for the sudden way in which it appears.

BIBLIOGRAPHY

DEBYE. "Polar Molecules."
FALKENHAGEN. *Reviews of Modern Physics*, **3**, 412 (1931).
KRAUS. "The Properties of Electrically Conducting Systems."
LEWIS and RANDALL. "Thermodynamics."
NEWMAN. "Electrolytic Conduction."
Transactions of the Faraday Society, **19**, 667 (1924); **24**, 334 (1927).
WALDEN. "Leitvermögen der Elektrolyte."

NAME INDEX

(*The numbers refer to pages*)

Abello, 112
Adam, 79, 83, 84, 85, 96
Aderhold, 186
Aharoni, 280
Akulov, 301, 320
Allen, H. S., 183
Allen, J. F., 360
Allin, 249
van Alphen, 261
Andrade, 92, 224
Appleton, 159, 160, 161, 163
Arkadiew, 304
Arsénieva, 15
van Aubel, 359
Auwers, 304

Bacher, 249
Back, 248
Bär, 181
Barfield, 161
Barker, 173
Barkhausen, 167, 303
Barrett, 160, 161
Bartell, 90
Bartlett, 363, 364
Basset, 55
Bates, 295, 296, 297, 306
Baudisch, 261, 304
Bauer, E., 279
Bauer, F., 358
Bauer, L. A., 334
Bazzoni, 201
Bearden, 200
Becker, 321
Beetz, 206
Békésy, 118
Benndorf, 333
Bethe, 17, 316
Bhagavantum, 188
Birch, 272
Birge, 206, 207
Birtwistle, 20
Bitter, 280
Bjerrum, 353
Black, 95
Blüh, 355
Blumentritt, 357
Boas, 16
Boch, 330
Bollinger, 356
Boltzmann, 25, 346
Bonhoeffer, 177
Boord, 174
Borelius, 157, 316
Born, 2, 3, 78
Bose, 23, 30
Bothe, 220, 231
Bourland, 275
Bowen, 193, 194
Boyce, 190
Boyle, 114
Bozorth, 304
Bragg, W. H., 8, 196, 205, 235
Bragg, W. L., 11, 205, 235
Breit, 160, 161, 163, 221
Brendel, 359
Brickwedde, 182
Bridgman, 55, 63, 64, 96, 114
Brillouin, 30, 54, 364
de Broglie, 3, 19, 20, 192, 196, 235
Browne, 97, 131
Brüche, 231
Brück, 249
Buckingham, 119, 235
Buckley, 68
Bühl, 16
Burch, 72, 73, 75
Busse, 167
Butterworth, 110

Cabannes, 183
Cabrera, 267, 275, 276
Cady, 105, 110
Cameron, 228, 230, 231, 232
Capel, 280
Carrad, 298
Chadwick, 226, 235
Chalonge, 335

Chantillon, 273
Chapman, 333, 334
Chase, 234
Chattock, 306
Chi-Sun-Yeh, 207
Clark, 328
Clausius, 156
Clusius, 178
Cochrane, 97
Cohen, 36, 261
Collet, 264
Compton, 190, 198, 206, 216, 217, 226, 235
Condon, 20
Constable, 20
Cork, 200
Cowperthwaite, 353
Curtis, 169
Czerny, 168, 173

Dadieu, 185
Dahl, 163
Darmois, 54
Darrow, 20, 54, 324
Darwin, 15, 209
Daure, 183, 185
Dauvillier, 16, 198, 199
Davis, A. H., 121, 142
Davis, B., 210, 211, 213
Davisson, 4, 11, 13, 14
Debye, 8, 153, 221, 222, 223, 325, 328, 329, 330, 340, 346, 348, 349, 353, 354, 356, 365
Defoe, 206
Dempster, 192
Dennison, 169
Deodhar, 183
Dershem, 216
Deubner, 359
Dillinger, 323
Dirac, 3, 15, 20, 24, 30, 32, 187, 221, 226
Doan, 198
Doane, 217
Dobson, 335
Dolejsek, 206
Dorfman, 249, 298, 323
Drude, 168
Duane, 207, 210
Dubois, 44
Dulong, 32
Dupérier, 275
Dupinay, 55
Dushman, 46, 69, 75, 96
Dye, 110

Eccles, 97, 159
Eddington, 208, 234, 237
Edlén, 193, 194
Edmondson, 77
Egerton, 76, 77
Einstein, 23, 30, 306, 330
Elias, 333
Ellett, 18
Ellis, C. D., 226, 235
Ellis, J. W., 175
Elsasser, 4
Elwell, 136
Emir, 84, 85,
van den Ende, 151, 154
Epstein, 231, 338
Ericson, 193
Errera, 331
Estermann, 17
Eucken, 153, 177
Ewald, 199
Ewing, 317, 322
Eyring, 50

Farry, 335
Fajans, 259, 354
Falkenhagen, 358
Faraday, 325
Farquharson, 260
Fermi, 24, 26, 30, 32, 33, 37, 249
Fessenden, 124
Fischer, 66
Fletcher, 142
Flint, 20
Focke, 261
Fœx, 272, 295, 324
Ford, 132
Forrer, 265, 288, 305
Forster, 216
Foster, 195
Found, 75
Fowler, 39, 41, 46, 50, 51, 53, 54, 297, 324
Fox, 167, 173
Fränz, 360
Frazer, 353
Frenkel, 364
Friedel, 90
Frilley, 225
Frumkin, 86, 89
Fucks, 329
Fürth, 41

[illegible]E, 67, 71
Gale, 233
Ganesan, 185

Ganguli, 89
Gans, 318
Gerlach, 243, 246, 247, 299, 309
Germer, 4, 11, 13, 14, 15
Gibbs, 84
Gill, 167
Gingrich, 220
Glagolewa-Arkadiewa, 166
Glaser, 260
Gleich, 234
Goetz, 260
Good, 223
Gossling, 51
Götz, 335
Goudsmit, 32, 248, 249
Gouy, 86, 87
Gowan, 104
Gray, F. W., 260
Gray, J. A., 226
Green, 163
Grimm, 255
Guastalla, 84
Gulik, 146
Gunn, 333, 334
Guthrie, 275
Guttinger, 249

DE HAAS, 261, 280, 306, 315, 316, 359, 361, 362
Ham, 205
Hammar, 260
Hardy, 79, 90, 92
Harteck, 177
Hartley, 344, 345, 353
Hartree, 258, 364
Hatley, 211
Hatschek, 92
Heaps, 304
Heck, 99
Hector, 253, 254, 279
Heisenberg, 2, 3, 20, 187, 302, 322
Hellmann, 355
Helmholtz, 86
Henning, 147, 150
Hess, 231
Heuse, 147, 150
Hevesy, 342
Hickman, 73
Hildebrand, 55
Hiller, 178
Hittorf, 342
Hjalmar, 210
Hoag, 192
Hoffmann, 226
Hogart, 259
Holgersson, 264
Holst, 150, 153
Honda, 291, 293, 300, 320
Housekeeper, 72
Houston, 37, 50, 364
Howe, 200
Howlett, 359
Hubbard, 113
Hückel, 340, 346, 348, 349, 353, 354, 356
Hughes, 202
Hulburt, 231, 333, 334, 338
Hull, 8
Hund, 270, 271, 275, 280, 307
Hunt, 200, 207

IDRAC, 332
Ikenmeyer, 255, 256, 259

JAANUS, 298
Jackson, D. A., 248, 249
Jackson, L. C., 272, 278
Jacobs, 254
Jacobsen, 329
James, 364
Jauncey, 221
Jeans, 232
Jevons, 169
Jessop, 84, 85
Joffe, 208
Joffé, 89
Joffre, 15
Johansson, 157
Johnson, 17
Johnstone, 330
Jona, 327
Jones, 356
Joos, 235, 255, 256, 259, 357
Jordan, 3

KALLMANN, 220
Kapitza, 297, 310, 314, 316, 363, 364
Kar, 89
Kaya, 290, 291, 293, 300, 308
Kaye, 96, 121, 142
Keesom, 71, 92, 145, 146, 147, 149, 151, 154, 156, 157, 222
Kellermann, 216
Kellström, 200
Kennedy, 234
Keyes, 329
Kikoin, 298
Kikuchi, 11
King, C. V., 354
King, R. W., 74

Kingdon, 42
Kirchner, 11
Kirkwood, 329
Klein, 187, 221, 226
Klinkhardt, 298
Knauer, 17
Knipping, 210
Knudsen, 78
Kohlrausch, 185, 351
Kolhörster, 231
Kossel, 276
Kösters, 43
Kramers, 187, 217
Kraus, 365
Krchma, 331
Krishnan, 182, 186
Kronig, 217, 327
Kung, 167

Landé, 241
Landsberg, 179, 186
Lane, 35, 117
Lange, 329, 331
Langer, 180
Langevin, 114, 250, 262, 263, 264, 325
Langmuir, 16, 42, 68, 77, 79, 82
Laporte, 307
Larmor, 163
Larrson, 212, 216
Lassen, 333
Laue, 12
Lauritsen, 50
Lawrence, 49
Lecomte, 235
Lehrer, 260
Lennard-Jones, 29, 53
Leu, 247
Lewis, 279, 365
Lichte, 100
Lindemann, 363
Lindsay, 142
Linford, 49
Loomis, 113
Lorentz, 217
Lorenz, 342
Lübcke, 100
Lugeon, 163
Lukirsky, 89
Lyman, 189, 190, 235

, 353
Mackay, 77
Madge, 95
Mandelstamm, 179, 186
Manebuck, 327
Mahajani, 319
Marcelin, 84
Maris, 333
Mark, 220
Mashiyama, 320
Mason, 142
Masumoto, 293
Mathews, 99
Matossi, 186, 235
Mayer, 78
McBain, 353
McKeehan, 302, 324
McLennan, 35, 36, 184, 249, 261, 329, 359, 360
Mees, 195
Meissner, 315, 316, 359, 360, 364
Mensing, 327
Menzies, 181, 183, 186
Merritt, 164
Meyer, 173
Michelson, 232, 233
Miles, 327
Miller, D. C., 233, 234
Miller, W., 90
Millikan, 50, 158, 193, 194, 228, 230, 231, 232, 338
Milne, 333
Milner, 345
Mirolubow, 364
Mittelstaedt, 359
Mizushima, 329
Molthan, 76
Morrell, 167
Morse, 20
Moseley, 205
Muller, 90

Nardroff, 211
Nayden, 355
Nernst, 29, 146, 153, 354
Newman, 76, 80, 96, 148, 340, 365
Nichols, 166, 330
Nishina, 221, 226
Nordheim, 41, 46, 50, 51
Norgaard, 147
Nowakowski, 83
Nusbaum, 261

Ogg, 331
Olson, 18
Onnes, 145, 146, 150, 153, 154, 156, 277, 279, 315, 316, 359, 360, 361, 363
Onsager, 354
Osgood, 200
Otto, 147

Overbeck, 266
Owen, 35

Palmer, H. H., 207
Palmer, W. G., 90
Paris, 121
Partington, 355
Pascal, 259
Paschen, 167
Patterson, 210
Pauli, 34, 35, 36, 254, 259, 267, 326, 327
Pauling, 258, 326
Peddie, 317, 324
Perrier, 279, 302
Peters, 182
Petit, 32
Phipps, 247
Piccard, 234, 279, 298
Pielemeier, 112
Pierce, 105, 109, 112
Planck, 1, 24
van der Pol, 133
Polednik, 44
Pollitzer, 154
Porter, 93
Potter, 294, 298
Powell, 302, 323, 324
Preisach, 304
Pringsheim, 179
Prins, 223

Rabinowitsch, 354
Raikes, 344, 345
Raman, 178, 186, 223, 261
Ramanathan, 223
Randall, 365
Rankine, 136
Rao, 185
Rasetti, 184
Rawlins, 173, 235
Regener, 229, 230
Reicheneder, 259
Reid, 112
Reisener, 342
Remy, 342
Rice, 54
Richardson, 43, 46, 47, 50, 201
Rideal, 84, 89, 173
Rieckhoff, 359
Rigi, 234
Roberts, 153, 157
Robertson, 167, 173
Rodebush, 77
Rosenfeld, 36
Rossi, 231
Rother, 51
Ruark, 20
Rubens, 167
Ruedy, 36, 261
Rule, 355
Rupp, 10, 14, 15, 16
Rutherford, 224, 226, 235
Rysselberge, 353

Sabine, 118
Sack, 355, 359
Sanford, 73
Sänger, 327
Sappenfield, 174
Sawyer, 18
Schæfer, 186, 235
Scheffers, 315, 316, 364
Schein, 216
Scherrer, 8, 222, 280
Schidof, 264, 266
Schmidt, 149
Schofield, 84, 86
Schottky, 50
Schrödinger, 2, 3, 4, 19, 20, 252, 270
Schubnikow, 315
Schüler, 249
Schulman, 89
Schumann, 189
Searle, 76, 80, 96
Serres, 264
Service, 99
Sharp, 220
Shearer, 90
Sheppard, 95
Siegbahn, 193, 197, 200, 206, 210, 212, 216, 235
Silsbee, 360, 362
Simpson, 339
Sixtus, 305
Sizoo, 304, 361
Skobelzyn, 226, 231
Slack, 213
Slater, 323
Smedt, 92, 222
Smith, 174
Smith-Rose, 161
Smyth, 327, 329
Snook, 72
Soné, 254, 279
Snow, 168, 173
Söderman, 193, 194, 201
Sommerfeld, 20, 31, 37, 38, 39, 45, 46 51, 52, 208, 243, 255, 267, 307
Stahel, 234

Stauss, 213
Steinke, 231
Stenström, 209, 210
Stephenson, 99
Stern, O., 17, 86, 243, 246
Stern, T. E., 52
Stewart, 139, 141, 142, 223
Stokes, 341
Stoner, 253, 258, 259, 273, 324
Sucksmith, 35, 294, 298, 306, 307
Swann, 234, 333

TÄNZLER, 254
Taylor, A. M., 168, 175, 235
Taylor, G. B., 114
Taylor, J. B., 18, 247, 249
Taylor, N. W., 279
Tear, 166, 330
Terrill, 210
Thibaud, 192, 199, 224, 225
Thomas, 117
Thompson, 113
Thomson, G. P., 7, 14, 16, 20
Thomson, J. J., 363
Thoraeus, 197, 199
Tolksdorf, 175
Tolman, 54
Tomaschek, 234
Tonaka, 223
Tonks, 305
Trillat, 83
Trivelli, 195
Tsuji, 223
Tucker, 101
van der Tuuk, 198
Tuve, 160, 161, 163
Tuyn, 316, 360, 361
Tyndall, 303

UHLENBECK, 32
Ulich, 341, 355
Urey, 20

VAUGHEN, 156
Venkateswaran, 185
van Vleck, 253, 258, 271, 280, 327
Voigt, 315
Voogd, 316, 359, 361, 362
de Vries, 77

WADLUND, 198
Walden, 354, 355, 365
Wall, 324
Waller, 212, 216, 364
Warren, 117
Watson, 119
Watt, 335
Weber, 147, 149
Webster, A. G., 134
Webster, W. L., 300, 308, 319, 320
Wegel, 117
Weiss, 258, 259, 264, 265, 276, 280, 288, 293, 294, 295, 298, 323, 324
Weigt, 327
Welo, 261, 276, 304
Wentzel, 217
Werner, 355
Whipple, 101
White, 249
Wiegland, 332
Wien, 356
Wiener, 3
Wiersma, 265
Wigner, 176
Wilhelm, 329, 359, 360
Williams, A., 324
Williams, J. W., 330, 331, 358
Wills, 253, 254, 279
Wilson, C. T. R., 220, 335, 338
Wilson, H. A., 19, 252
Witmer, 176
Wolf, 15
Woltjer, 265, 277
Woo, 221
Wood, A. B., 97, 131, 132
Wood, R. W., 180, 184, 190
Woods, 53

ZAHL, 18
Zahn, 327, 355
Zernicke, 223
Zumstein, 198
Zwicky, 208

SUBJECT INDEX

(*The numbers refer to pages*)

Absorption of cosmic rays, 228
  of gamma rays, 225
  of sound, 119, 120
Accommodation coefficient, 78
Acoustical impedance, 134, 140, 142
  line, 139
Acoustics, 97
  architectural, 118
  of the ear, 117
Additional resistance, 315
Adsorption, ionic, 86, 88
  on solids, 90
Air waves, propagation of, 101
Akulov's theory of ferromagnetism, 320
American system of sea-depth measurement, 124, 126
Amplification of sound, 122
Angle of descent, sound, 101
  of incidence method, wireless, 161
Anomalous dispersion of X-rays, 200
Anti-Stokes' lines, 178, 182
Atmosphere, ionic, 347
Atmospheric electricity, 331
  ionisation, 158, 162, 163, 166, 332
  ozone, 335
  waves, 159
Atom, magnetic moment of,
    diamagnetic, 250
    ferromagnetic, 287
    paramagnetic, 240
Atomic heats, 32, 152
  nucleus, magnetic moment of, 248
  orientation, 242
  rays, magnetic deflection of, 242
  susceptibility, 252
Atoms, angular momentum of,
  magnetic properties of, 236
  states of, 236
  wave characteristics of, 17
Audibility zones, 101, 103
Avogadro's constant, 206, 208

Band pass wave filter, electrical, 139
Band spectra, branches of, 172
Band spectra, infra-red, 168
    oscillation, 169
    oscillation-rotation, 171
    rotation, 169
Barkhausen effect, 303
Becker's theory of ferromagnetism, 321
Binaural compensator, 126
Bohr magneton, 240, 241, 246, 248, 249, 269, 299
Boltzmann's constant, 25
Bose-Einstein statistics, 23
Bragg's formula for specular reflection, 8, 13, 209
British system of sea-depth measurement, 129

Calorimeter method for X-ray wavelengths, 204
Capillary curve, 87
Change of state, pressure effect, 61
Characteristic X-rays, 201
Classical statistics, 23
Clausius-Mossotti relation, 325, 326
Cold discharge, 50
Complex ions, susceptibility of, 276
Compliance, 140
Compressibility pressure effects, 56, 58, 60, 62
Compton effect, 1, 217, 226
Condensed films, 84
  layer, ionic, 87
Conduction dispersion, 358
  electrical, of metals, 37, 311
    in intense magnetic fields, 311
  electrolytic, 339
    theories of, 345
  thermal, of metals, 37
Conductivity, equivalent, 340
Constants, physical. *See* Physical Constants.
Contact potential difference, 40
Corpuscular rays, 231
Cosmic rays, 226
    absorption of, 228

Cosmic rays, nature, 231, 338
    origin, 228
    wave-length, 229
Critical field, 313
  potential, 203
  temperature of ferromagnetics, 282
Crystal structure of ferromagnetics, 291
Crystals, compressibility of, 60
  diamagnetism of, 260, 266
  diffraction of electrons, 4
    of X-rays, 196
    of γ-rays, 225
  number of molecules per cubic centimetre in, 206
  paramagnetism of, 266
  single, magnetisation of, 290
    magneto-resistance in, 308
  structure of, 91, 196, 205
Curie-point (temperature), 265, 268, 288
    of ferromagnetics, 285, 293, 299, 302, 323
Curie's constant, 264, 268
  law, 263
Curie-Weiss law, 265, 268, 272, 275, 280
Cybotapis, 223

Debye's constant of specific heat, 153
  equation for polarisation, 326, 327, 329
  theory of electrolytic conduction, 346
    of specific heats, 153
Degeneracy of a gas, 24, 29, 132
Depolarisation of light, 183
Depths at sea, measurement of, 124, 126, 128, 129
Diamagnetic moment of atom, 247, 250
Diamagnetism, 250
  of crystals, 260
  of gases, 254
  of ions, 256
  of molecules, 259
  of paramagnetic elements, 261
  of solutions, 255
  theory of, 250
Dielectric constant, 325
    of electrolytic solutions, 87, 354
    of gases, 327
    of liquids, 329
    variation with frequency, 329
Diffraction bands in liquids, X-ray, 92, 222
  of electrons, 2, 4, 13, 15
    applications, 15
  of X-rays, 5, 7, 90, 196
    with crystals, 196
    with gratings, 5, 7, 198
Diffuse double-layer, 86
Dipole, 325
Dispersion curves, X-rays, 216
  in electrolytic solutions, 358
  of X-rays, 216
Distribution function, 22, 24, 27, 29
    for degenerate gas, 26
    for electron gas, 33, 45, 49
    Maxwellian, 27, 29, 45
Domains, magnetic, 280, 284, 304
Doublet, electrical (dipole), 325
    permanent, 325, 326
Drift of ether, 233
Duane-Hunt law, 207

Ear, acoustics of, 117
Echo ranging and sounding, 124
Echos, wireless, 165
Effusion of gases, 77
Elasticity, pressure effect on, 63
Electric waves, 158
    ultra-short, 166
Electrical charge, unit of, 206
  conduction of metals, 37
      in strong magnetic fields, 311
    pressure effect on, 64
  moment at interfaces, 87
    of molecules, 325
  resistance, theory of, 37, 66, 364
  wave filters, 137
Electricity, atmospheric, 331
  conduction of through solutions, 339
Electrification at interfaces, 86
Electro-acoustics, 133
Electrolytes, strong, theory of, 349
Electrolytic conduction and concentration, 351
  solutions, theory of, 339, 345
    dielectric constant of, 354
    dispersion of, 358
Electromagnetic radiations, 158
Electromotive force and ferromagnetism, 299
Electron emission in strong magnetic fields, 50
  gas, 31
    Fermi distribution, 33, 45, 49
    susceptibility of, 35
  spin, 32, 237, 248
  theory of metals, 30
  waves, 4, 37
    existence of, 19
    polarisation of, 14
Electrons, diffraction of, 2, 4, 13, 15
    applications, 15

Electrons, high speed, 231
  interaction of, 53
  recoil of, 218
  reflection of, 10. *See also* Diffraction of Electrons.
  refraction of, 11
  specific heat of, 31, 33
e/m, values of, 208
Energy states, 24, 27, 187, 236,246
  zero point, 25, 29, 32
Equivalent conductivity, 340, 352
Ether drift, 233
Ewing's theory of ferromagnetism, 317
Expansion of ferromagnetics, 302
  thermal, pressure effect on, 59
External work function, 41

Fading of wireless reception, 160
Fermi-Dirac statistics, 24
    applications of, 26, 30, 37, 38, 39, 45, 48, 51, 52
    distribution function, 26, 33
Ferromagnetics, anomalous expansion of, 302
  atomic moments of, 287
  Barkhausen effect, 303
  change to paramagnetics, 285
  crystal structure of, 291
  electromotive force of, 299
  gyromagnetic effect, 306
  magneto-mechanical phenomena, 300
    resistance phenomena, 307
    thermal phenomena, 293
  specific heat of, 293
Ferromagnetism and temperature, 283
  theories of, 280, 316
Fessenden method of sea-depth measurement, 124
Films, 79
  condensed, 84
    gas, 83
  liquid-expanded, 84
  orientation of molecules in, 82, 83, 90
Filters, wave, acoustical, 139, 141
    electrical, 136, 138, 139, 140
Fish tracks, 220
French system of sea-depth measurement, 128
Function, distribution, 22
  external work, 41

Gadolium sulphate, susceptibility of, 275, 277, 310
Gaede's mercury vapour pump, 69
Gamma rays, 224
Gans' theory of ferromagnetism, 318
Gas, degeneracy of, 24, 29
  distribution, function of, 26
  electron, 30
  film, 84
  flow of, at low pressures, 76
Gases, dielectric constant of, 327
  effusion of, 77
  electrical moments, 328
  infra-red spectra, 173
  pressure effects, 56
  Raman effect, 183
  susceptibility of, 254, 279
  velocity of sound in, 104
Gauge, ionisation, 74, 76
  Knudsen's, 148
Gerlach and Stern's experiment, 244
German method of sea-depth measurement, 124
Ground wave, 159, 166
Group-retardation method, wireless, 161
Gyromagnetic effect, 306

Heaviside layer. *See* Kennelly-Heaviside Layer.
Heisenberg's theory of ferromagnetism, 302, 322
Helium, liquid, vapour pressure, 149
  solid, melting-point temperature, 147
High-frequency pass, acoustical wave filter, 141
    electrical wave filter, 139
  vibrations, 104
  waves, properties of, 114
High-pressure effect on change of state, 61
    on compressibility, 56, 60
    on elasticity, 63
    on electrical resistance, 64
    on gases, 56
    on liquids, 58
    on solids, 60
    on thermal conduction, 63
      electromotive force, 66
      expansion, 59
    viscosity, 62
High-vacuum pumps, mercury, 67
    oil, 72
  technique, 67
Horns, theory of, 134
Hot-wire microphone, 101
Hydrogen, two types of, 176, 184
Hydrophones, 97
Hyperfine structure of lines, 248, 249

Ideal resistance, 315
Impedance, acoustic, 134, 140, 142
Inertance, 140
Infra-red spectra, 167
  bands, oscillation, 167
    oscillation-rotation, 171
    rotation, 169
    theory of, 169
  of gases, 173
  of liquids, 174
  of solids, 175
Inner quantum number, 239
Intense magnetic fields, 309
    and electrical conduction, 311
Intensity of scattered radiation, 220
  of sound, 115
Interaction of electrons, 53
Interface, electrical moment of, 87
Interfacial electrification, 86
  orientation of molecules, 82, 90
Interferometer, ultra-sonic (high-frequency), 113
Interionic forces, 345, 346, 356
Internal magnetic field, 265
International temperature scale, 143
Intrinsic potential difference, 40
Ionic adsorption, 86, 88
  atmosphere, 347, 357
Ionisation gauge, 74, 76
  in atmosphere, 158, 162, 163, 166, 332
  in solutions, 185, 340, 349, 353
Ions, radius of, 341, 343, 344
  solvation of, 340
  susceptibility of, 256, 271

Kennelly-Heaviside layer, 158
    height of, 160, 162, 334
  layers, 163
Knudsen gauge, 148
Kossel's law, 276

Landé splitting factor, 241
Langevin's function, 263
  theory of paramagnetism, 262, 267, 276
Larmor precession, 238, 250
Light, velocity of, 232
Lightning, 339
Liquid-expanded films, 84
Liquids, dielectric constant of, 329
  diffraction of X-rays in, 222
  infra-red spectra of, 174
  pressure effect, 58
  Raman effect in, 185
  velocity of sound in, 97, 113
  viscosity of, 92

Low-pass acoustical wave filters, 140
  electrical wave filters, 138
Low pressures, flow of gas at, 76
    measurement of, 74, 76, 148
    production of, 67
  temperatures, 145, 147
    specific heat at, 152
Lubrication, 92

Macroscopic state, 21
Magnetic domains, 280, 284, 304
  fields, emission of electrons in, 50
    intense, 309
      effect on electrical resistance, 311
        superconductivity, 360
Magnetic moment of atom, 251
    of nucleus, 248, 249
  properties of atoms, 236
  quantum number, 238
  susceptibility, 250
  threshold valve, 360
Magnetisation of single crystals, 290
  spontaneous, 281, 283
Magnetism, 236
Magneto-mechanical effects, 300
Magneton (Bohr), 240, 246, 248, 249, 260, 270, 299
  (Weiss), 267, 270, 273, 287, 307
Magneto-resistance effects, 307
Magnetostriction, 300, 305, 320, 322
Magneto-thermal phenomena, 293
Mahajani's theory of ferromagnetism, 319
Manometers for low pressures, 74, 148
Mass susceptibility, 252, 263
Matter waves, 4
  wave-like characteristics of, 1
Maxwellian distribution, 27, 29, 45
Mechanics, quantum, 2
  statistical, 21
Melting-point temperature of solid
    helium, 146
    hydrogen, 147
Mercury vapour pumps, 67
Metals, electron theory of, 30
  para-susceptibility of, 34
  vapour pressure of, 77
Michelson-Morley experiment, 233
Microphone, hot-wire, 101
Micro-residual resistance, 362
Microscopic state, 21
Molecular magnetic field, 265
  polarisability, 326
  susceptibility, 250, 256, 263

Molecules, diamagnetism of, 259
  electric moment of, 328
  polarised, 325
  wave characteristics of, 17

Navigation of ships, 129, 132
Nernst's heat theorem, 29
New statistics, 23
Nucleus, magnetic moment of, 248, 249
Nul-point energy, 25, 29, 32

Oceanic type of echo-sounding apparatus, 130
Oil pumps, high vacuum, 72
Optical recording of sound, 135
Orientation of atoms in space, 242
  of molecules, 326, 330, 354
  of molecules in films, 82
Ortho-hydrogen, 176, 184
Oscillation bands in infra-red, 169
  rotation bands, 171
Oscillator, piezo-electric, 111
Ozone in atmosphere, 335

Para-hydrogen, 176, 184
Paramagnetic elements, diamagnetism in, 261
Paramagnetics, gyromagnetic effect in, 307
Paramagnetism, 262
  of ions, 271
  of metals, 34
  of salts, 272
  theory of, 263, 267
Paschen-Back effect, 240
Peddie's theory of ferromagnetism, 317
Peltier coefficient, 52
Phase space of a system, 22
Photomicrography, 194
Phonic chronometer, 132
Photo-electricity, 47
Photo-electric method for X-ray wave lengths, 201
  threshold, 48
Photons, 1, 2, 19, 232
Physical constants, 205
Piezo-electricity, 104
Piezo-electric oscillator, 111
  resonator, 108, 109
  stabiliser, 110
Planck's constant, 1, 24
Platinum thermometry at low temperatures, 150
Polarisation of electron waves, 14
  of media, 325
Potential difference, 39, 40
    at interfaces, 86
    effect in electrolytes, 356
Pressure, surface, 83
Pressures, high. *See* High Pressures.
  low, measurement of, 74
    production of, 67
Primary spreading, 80
Propagation of air waves, 101
Pumps, high vacuum, 67

Quantum mechanics, 2
  numbers, 237, 242
Quartz oscillator, 109, 111
  plates, high-frequency vibrations in, 104
  resonator, 107, 109
  stabiliser, 110

Radiations, electromagnetic, 158
Radio-acoustical method of sound-ranging, 131
Raman effect, 178
    in gases, 183
    in liquids, 185
    in solids, 186
    technique of, 180
    theory of, 186
  lines, intensity of, 182
    width of, 183
Range of electromagnetic radiations, 158
  of explosive sounds, 100
Ranging, sound, 123
Recoil of electrons, 218
Reflection method of depth measurement at sea, 126
  of electrons. *See* Diffraction of Electrons.
Refraction of electrons, 11
  of wireless waves, 158
  of X-rays, 200, 209, 210
Refractive index of crystals, 200
Relaxation, electric force of, 357
  oscillation, 133
  time of, 330, 357
Reproduction of sound, 135
Resistance, electrical, additional, 315
    at low temperatures, 150, 359
    ideal, 315
    in strong magnetic fields, 312
    pressure effect on, 64
    theory of, 364
  micro-residual, 362

Resonator, piezo-electric, 109
  quartz, 107, 109
  steel, 110
Reverberation, theory of, 118
Rocking curves, 213
Rotation bands in infra-red, 169
Rydberg's constant, 207

Salting-out process, 340
Scattered radiation, intensity of, 220
Scattering of X-rays, 217
  of γ-rays, 226
Sea, velocity of sound in, 97
Sea-depths, measurement of, 124
Secondary spreading in films, 80
Sensation, scale in sound, 116
Single crystals, excitation of X-rays from, 204
    magnetisation of, 290
    magneto-resistance effects, 308
    susceptibility of, 260
Soft X-rays, 201
Solid helium, 146
  hydrogen, 146
Solids, adsorption on, 90
  effect of pressure on, 60
  infra-red spectra of, 175
  Raman effect in, 186
Solutions, conduction of electricity in, 339
  susceptibility of, 255
Solvation of ions, 340
  numbers, 342
Sound, absorption of, 120
  amplification of, 122
  intensity of, 115
  optical recording of, 135
  ranging, 123, 124, 126, 131
  reproduction of, 135
  sensation scale, 116
  velocity of, in gases, 104, 112
    in liquids, 97, 113
Sounds of long range, 100
  masking of, 117
Space quantisation of magnetic numbers, 243
Specific heat, 29, 32
    at low temperatures, 152, 153
    of electrons, 31, 33
    of ferromagnetics, 293
Spectra, infra-red, 167
    bands, branches of, 172
      oscillation, 169
      oscillation-rotation, 171
      rotation, 169
Spectra, of gases, 173
    of liquids, 174
    of solids, 175
  overlapping of ultra-violet and X-ray, 194
  ultra-violet, 188, 193
Spectrographs for ultra-violet region, 189, 193, 197, 199
Spin of electron, 32, 34, 237, 248
Splitting factor, 241
Spontaneous magnetisation, 281, 283
Spreading of films, 79
Stabiliser, piezo-electric, 110
State, or phase, space of a system, 22
  change of, effect of pressure on, 61
States, energy, 24, 187, 236, 246
Statistical mechanics, 21
Statistics, Bose-Einstein, 23
  classical, 23
  comparison of, 29
  electron theory of metals, 30
  Fermi-Dirac, 24
    applications of, 26, 34, 37, 39, 45, 47, 50, 51
Stokes' law, 341, 343
  lines, 178, 182
Superconductivity, 37, 359
  effect of magnetic field on, 360
  of alloys, 359, 362
  theory of, 363
Surface films, 79, 89
  pressure, 83
  tension, 79
Susceptibility (diamagnetic), 250
    and electron structure, 36, 254
    atomic, 252, 263
    experimental results, 253
    ionic, 256
    mass, 252, 263
    molecular, 256
    of crystals, 260
    of gases, 254
    of ions and atoms, 253, 257, 271
    of solutions, 255
    variation with direction, 261
    volume, 252, 263
Susceptibility (paramagnetic), 34
    at low temperatures, 276
    of complex ions, 276
    of gases, 279
    of metals, 34, 35
    of salts, 272
    of rare earths, 275
    variation with direction, 266

Susceptibility (ferromagnetic), 283
  atomic moments of ferromagnetics, 287, 306
  critical temperature, 282
  spontaneous magnetisation, 281, 283
  temperature effects, 285
  theory of, 281
  variation with direction, 290, 300

Temperature scale, international, 143
Temperatures, low, 145, 147
    specific heat at, 152
  melting point of solid helium, 146
      hydrogen, 146
  standard, 144, 147
Thermal conduction in metals, 37
    pressure effects, 63
  expansion, effect of pressure on, 59
  transpiration, 148
Thermionic constants, 43
Thermionics, 45
Thermo-couples at low temperatures, 149
Thermo-electric force at very low temperatures, 150
  phenomena, 51
    pressure effects, 66
Thermometry, platinum, at low temperatures, 150
Thomson coefficient, 53
    at low temperatures, 156
Threshold current, 360
  magnetic, 360
Thunderclouds, 335
Thunderstorms, 337
Total reflection of X-rays, 198, 216
Transference numbers, 342
Transmission unit, 116
Transport of water, 342

Ultra-short wireless waves, 166, 167
Ultra-sonic interferometer, 113
  waves, 112, 114. *See also* High-Frequency Waves.
Ultra-violet photomicrography, 194
  region of spectrum, 188, 193, 194
Undograph, 102
Unit of electrical charge, 206
  transmission, 116

Vacuum spectrograph, 189, 193, 197, 199
Vapour pressure of liquid helium, 149
    of metals, 77
Velocity of light, 232
  of sound in gases, 104, 112
  of sound in liquids, 97, 113
  of sound variation with frequency, 114
Vibration, measurement of amplitude of, 117
Vibrations, high-frequency, 104
Viscosity of liquids, 92
  pressure effects, 62
Volta effect, 40
Volume susceptibility, 252, 263

Water transport, 342
Wave filters, acoustical, 139
    electrical, 136
Wave-lengths, ultra-violet, 193
  X-rays, 196, 198, 201, 204
Wave-like character of atoms, 17
    of electrons, 4
    of matter, 1
Wave mechanics. *See* Quantum Mechanics.
  packets, 19
Waves, electric, 158, 159
  electron, 2, 4, 11, 14, 15, 19, 37
  matter, 1, 4, 19
  ultra-sonic (high-frequency), 112, 114
Wien effect, 356
Wireless echoes, 165
  wave front, structure of, 164
  waves, 158, 166, 167
    fading of, 160

X-rays, diffraction of, 5, 7, 90, 91, 196, 222
    of in liquids, 92, 222
  dispersion, 216
  excitation of characteristic, 201
  refraction of, 200, 209, 210
  scattering of, 217
  soft, 201
  total reflection of, 198, 216
  wave-lengths, 196, 198, 201, 204

Zeeman effect, 238, 240, 246, 248
Zero-point energy, 25, 29, 32
Zones of audibility, 101, 103
  of silence, 100

BOOKS ON
NATURAL SCIENCE

Published by

J. & A. CHURCHILL LTD.

INDEX TO SUBJECTS

Analysis . . . 2—7
Bacteriology . 12
Biochemistry . 13
Botany . . . 9
Chemistry . . 2—7
Hygiene . . 14, 15
Microscopy . 15
Pharmacognosy and Materia Medica . . 10, 11
Pharmacy . . 10, 11
Physics . . . 8
Miscellaneous . 15

London:
40 Gloucester Place, Portman Square
W.1

COLLOID ASPECTS OF FOOD CHEMISTRY AND TECHNOLOGY

By WILLIAM CLAYTON, D.Sc., F.I.C., Chief Chemist and Bacteriologist to Messrs. Crosse & Blackwell Ltd. (London). 64 Illustrations. 580 pp. Royal 8vo. 36s. (1932)

ALLEN'S COMMERCIAL ORGANIC ANALYSIS

Written by specialists on each subject.

Fifth Edition. Edited by C. AINSWORTH MITCHELL, D.Sc., M.A., F.I.C., Editor of *The Analyst;* Consulting Chemist, London,

S. S. SADTLER, S.B., and E. C. LATHROP, A.B., Ph.D.

Vol. I. Introduction. Alcohols. Yeast, Malt and Malt Liquors. Wines and Potable Spirits, Neutral Alcohol Derivatives, Sugars, Starch and its Isomerides, Paper and Pulp-Testing. Aliphatic Acids. 804 pp. 8vo. 103 Figures. 32s. (1924)

Vol. II. Fixed Oils, Fats and Waxes, Special Characters and Methods, Butter Fat, Lard, Linseed Oil, Higher Fatty Acids, Soaps, Glycerin, Wool Fat, Wool Grease, Suint, Degras, Sterol Alcohols. 820 pp. 8vo. 24 Figures. 32s. (1924)

Vol. III. Hydrocarbons, Bitumens, Naphthalene and its Derivatives, Anthracene and its Associates, Phenols, Aromatic Acids, Gallic Acid and its Allies, Phthalic Acid and the Phthaleins, Modern Explosives. 742 pp. 8vo. 36 Figures. 32s. (1925)

Vol. IV. Special Characters of Essential Oils, Resins, India-Rubber, Guttapercha, Balata and Allied Substances, Constituents of Essential Oils and Allied Substances, General Characters and Analysis of Essential Oils. 658 pp. 8vo. 32s. (1926)

Vol. V. Tannins, Writing, Stamping, Typing, Marking and Printing Inks; Amines and Ammonium Bases, Analysis of Leather, Colouring Matters of Natural Origin, Colouring Substances in Foods, Benzine and its homologues, Aniline and its Allies, Naphthylamines, Pyridine, Quinoline and Acridine Bases. 712 pp. 8vo. 8 Figures. 32s. (1927)

Vol. VI. Colorimetry, Dyes and Colouring Matters, The Synthetic Dye-Stuffs, Analysis of Colouring Matters. 667 pp. 8vo. 5 Figures. 32s. (1928)

Vol. VII. General Introduction to the Alkaloids, Vegetable Alkaloids, Aconite, Berberine, Caffeine, Tea and Coffee, Cinchona Alkaloids, Cocaine, Cocoa and Chocolate, Opium Alkaloids, Strychnos Alkaloids, Tobacco and Nicotine, Tropine Alkaloids. 682 pp. 12 Figures. 32s. (1929)

Vol. VIII. Glucosides and Non-Glucosidal Bitter Principles, Enzymes, Putrefaction Bases, Animal Bases, Animal Acids, Cyanogen Compounds, Proteins, Digestion Products of Proteins. 772 pp. 35 Figures. 32s. (1930)

Vol. IX. Proteins of Plants, Proteins of Milk, Milk and Milk Products, Meat and Meat Products. 626 pp. 25 Figures. 32s. (1932)

Vol. X. Hæmoglobin and its Derivatives, Albuminoids or Scleroproteins, Structural Proteins, Examination of Foodstuffs for Vitamins, The Hormones, The Identification of Woods, The Pectic Substances, General Index to Ten Volumes. 818 pp. 72 Figures. 32s. (1933)

A Chemical Dictionary. Containing the words generally used in Chemistry, and many of the Terms used in related sciences.

By INGO W. D. HACKH, Professor of Chemistry, College of Physicians and Surgeons, San Francisco. Large 8vo, 790 pp. 232 Illustrations. Over 100 Tables. 45s. (1930)

The Chemistry, Flavouring and Manufacture of Chocolate Confectionery and Cocoa.

By H. R. JENSEN, M.Sc., F.I.C., Formerly Chairman of Consultative Panel, British Research Association for Cocoa, etc. 23 Illustrations. 422 pp. Royal 8vo. 27s (1931)

CLOWES AND COLEMAN'S QUANTITATIVE CHEMICAL ANALYSIS

Thirteenth Edition. Revised by D. STOCKDALE, Ph.D., A.I.C., University Demonstrator in Chemistry, Cambridge, and J. DEXTER, B.Sc., A.I.C. 133 Illustrations. 619 pp. 8vo. 18s. (1931)

ELEMENTARY PRACTICAL CHEMISTRY AND QUALITATIVE ANALYSIS

By FRANK CLOWES, D.Sc.Lond., and J. BERNARD COLEMAN, Assoc.R.C.Sci.Dublin.

Seventh Edition. Part I. **General Chemistry.** 258 pp. Post 8vo. 6s. Illustrations. (1920)

ELEMENTARY ANALYTICAL CHEMISTRY

(F. CLOWES and J. B. COLEMAN)

12th Edition revised by C. G. LYONS, M.A., Ph.D., Lecturer in Chemistry, Bradford Technical College, and F. N. APPLEYARD, B.Sc., F.I.C., Ph.C., Head of the Pharmacy Dept., Bradford Technical College. 256 pp. Crown 8vo. 6s. (1934)

Oils, Fats and Fatty Foods.

Their Practical Examination. A Handbook for Analytical and Technical Chemists.

By E. RICHARDS BOLTON, F.I.C., F.C.S., Consulting Technical Chemist. With Chapter on Vitamins by Professor J. C. DRUMMOND, D.Sc. Second Edition. 12 Plates and 34 Text-figures. 432 pp. Royal 8vo. 30s. (1928)

Theoretical Organic Chemistry.

By FRANCIS ARNALL, Ph.D., and FRANCIS W. HODGES, M.Sc., Senior Science Master at Coopers' Company School, London.

Part I. 30 Illustrations and 115 Experiments. 384 pp. 8vo. 10s. 6d. (1926)

Part II. 338 pp. 8vo. 12s. 6d. (1927)

The Chemistry of the Proteins and its Economic Applications.

By DOROTHY JORDAN LLOYD, D.Sc., F.I.C., Biochemist, British Leather Manufacturers' Research Association. Introduction by Sir F. G. HOPKINS, F.R.S. 292 pp. 8vo. 50 Illustrations. 10s. 6d. (1926)

The Chemical Analysis of Foods.

A Practical Treatise on the Examination of Foodstuffs and Detection of Adulterants.

By H. E. COX, M.Sc., Ph.D., F.I.C., Analytical and Consulting Chemist. 38 Illustrations. 332 pp. 8vo. 18s.

THE NATURAL ORGANIC TANNINS

History: Chemistry: Distribution

By M. NIERENSTEIN, D.Sc., Reader in Biochemistry, of Bristol. With a chapter on the Botany of Tannins by SKENE, D.Sc. 326 pp. Demy 8vo. 21s. (1934)

J. & A. CHURCHILL LTD.

PARRY'S CYCLOPÆDIA OF PERFUMERY

Describing the Raw Materials used by the Perfumer, their Origin, Properties, Characters and Analysis.

By E. J. PARRY, B.Sc., F.I.C., F.C.S., Analytical and Consulting Chemist.
2 Vols. 846 pp. Royal 8vo. 36s. (1925)

TREATISE ON GENERAL AND INDUSTRIAL CHEMISTRY

Bv Dr. ETTORE MOLINARI, Professor of Industrial Chemistry, Royal
Translated by T. H. POPE, B.Sc., F.I.C., A.C.G.I.
Second Edition. Translated from the fourth revised
edition. 328 Illustrations and 2 Plates. 896 pp. 8vo.
42s. (1920)

Vol. II. **Organic.** Second Edition. Translated from the third enlarged and revised Italian edition. Part I. 254 Illustrations. 472 pp. 8vo. 30s. (1921)
Part II. 303 Illustrations. 450 pp. 8vo. 30s. (1923)

TREATISE ON APPLIED ANALYTICAL CHEMISTRY

Edited by Professor VITTORIO VILLAVECCHIA, assisted by Nine Specialists. Translated by T. H. POPE, B.Sc., F.I.C., A.C.G.I.
Vol. I. 58 Illustrations. 492 pp. 8vo. 21s.
Vol. II. 105 Illustrations. 552 pp. 8vo. 25s. (1918)

Laboratory Manual for the Detection of Poisons and Powerful Drugs.

By Dr. W. AUTENRIETH, Professor in the University of Freiburg I.B. Authorised Translation by WILLIAM H. WARREN, Ph.D. Sixth Edition, translated from Fifth German Edition. 60 Illustrations. 724 pp. 8vo. 32s. (1928)

Practical Chemistry.

By WILLIAM G. VALENTIN, F.C.S. Tenth Edition. By Dr. W. R. HODGKINSON, F.R.S.E. 95 Engravings and Map of Spectra. 496 pp. 8vo. 12s. 6d. (1908)

A Text-book of Organic Chemistry.

By E. DE BARRY BARNETT B.Sc., A.I.C. 15 Illustrations. 392 pp. 8vo. 10s. 6d. (1920)

Industrial Organic Analysis, for the Use of Technical and Analytical Chemists and Students.

By PAUL S. ARUP, B.Sc., F.I.C. Second Edition. 25 Illustrations. 484 pp. Crown 8vo. 12s. 6d. (1920)

Manual of Chemical Technology.

By RUDOLF WAGNER, Ph.D. Second English Edition. Translated and Edited by Sir WM. CROOKES, F.R.S. 596 Engravings. 992 pp. Royal 8vo. 36s. (*Reprinted* 1904)

A Text-Book of Practical Chemistry.

By G. F. HOOD, M.A., B.Sc., and J. A. CARPENTER, M.A. 162 Illustrations. 540 pp. Royal 8vo. 21s. (1921)

CATALYSIS AND ITS INDUSTRIAL APPLICATIONS

By E. B. MAXTED, D.Sc.(Lond.), Ph.D.(Berlin), F.I.C., Special Lecturer in Catalysis in the University of Bristol. 225 Tables and 66 Illustrations. 538 pp. Royal 8vo. 36s. (1933)

TEXT-BOOKS OF CHEMICAL RESEARCH ENGINEERING

Edited by W. P. DREAPER, O.B.E., F.I.C.

Clouds and Smokes. The Properties of Disperse Systems in Gases.

By W. E. GIBBS, D.Sc., Professor of Chemical Engineering, University College, London. 31 Illustrations. 254 pp. 8vo. 10s. 6d. (1924)

The Theory of Emulsions and their Technical Treatment.

By W. CLAYTON, D.Sc., F.I.C. Foreword by Professor F. G. DONNAN, C.B.E., D.Sc., F.R.S. Second Edition. 42 Illustrations. 296 pp. 8vo. 15s. (1927)

Molecular Physics and the Electrical Theory of Matter.

By J. A. CROWTHER, Sc.D., F.Inst.P., Professor of Physics, University College, Reading. Fourth Edition. 34 Illustrations. 212 pp. Crown 8vo. 7s. 6d. (1927)

Notes on Chemical Research.

By W. P. DREAPER, O.B.E., F.I.C. Second Edition. 212 pp. 7s. 6d. (1920)

An Introduction to the Physics and Chemistry of Colloids.

By EMIL HATSCHEK. Fifth Edition. 22 Illustrations. 198 pp. Crown 8vo. 7s. 6d. (1925)

Catalysis and its Industrial Applications.

By E. JOBLING, *M.C.*, A.R.C.Sc., B.Sc., A.I.C. Second Edition. 12 Illustrations. 152 pp. Crown 8vo. 7s. 6d. (1920)

Catalytic Hydrogenation and Reduction.

By E. B. MAXTED, D.Sc., Ph.D., F.C.S. 12 Illustrations. 112 pp. Crown 8vo. 5s. (1919)

The Atmospheric Nitrogen Industry.

By Dr. BRUNO WAESER. Translated by E. FYLEMAN, B.Sc., Ph.D. In 2 Volumes. 72 Illustrations. 772 pp. 8vo. 42s. (1926)

Colloid Chemistry of the Proteins.

By Professor Dr. WOLFGANG PAULI, Director for Physico-Chemical Biology, University of Vienna. Translated by P. C. L. THORNE, M.A., A.I.C. 27 Diagrams and numerous Tables. 152 pp. 8vo. 8s. 6d. (1922)

Laboratory Manual of Elementary Colloid Chemistry.

By EMIL HATSCHEK. Second Edition. 21 Illustrations. 154 pp. Crown 8vo. 7s. 6d. (1925)

The Formation of Colloids.

By THE SVEDBERG, Professor of Physical Chemistry, University of Upsala. 22 Illustrations. 132 pp. Crown 8vo. 7s. 6d. (1921)

Ammonia and the Nitrides, with special reference to their Synthesis.

By E. B. MAXTED, D.Sc., Ph.D., F.C.S. 16 Illustrations. 124 pp. Crown 8vo. 7s. 6d. (1921)

Reagents and Reactions.

By EDGARDO TOGNOLI, Professor in the University of Modena. Translated from the Italian by C. AINSWORTH MITCHELL, D.Sc., F.I.C. 236 pp. F'cap. 8vo. 7s. 6d. (1918)

The Chemistry of Cyanogen Compounds and their Manufacture and Estimation.

By HERBERT E. WILLIAMS. 432 pp. 8vo. 12s. 6d. (1915)

J. & A. CHURCHILL LTD.

RECENT ADVANCES IN ANALYTICAL CHEMISTRY

Edited by C. A. MITCHELL, D.Sc., M.A., F.I.C.

Vol. I. **Organic.** Sugar Analysis—Oils and Fats—Essential Oils—The Proteins (with Biological Analysis of Proteins)—Tannins—Cereals—Milk and Milk Products—Paper—Petroleum and its Hydrocarbons—Coal—Gas. 432 pp. 25 Illustrations. 15s. (1930)

Vol. II. **Inorganic.** Hydrogen-ion Concentration—Common Metals—Rare Earth Metals—Platinum Metals—Microchemical Analysis—Water. 450 pp. 26 Illustrations. 15s. (1931)

Elementary Qualitative and Volumetric Analysis—Inorganic and Organic. For Medical, First Year University Science Students and Students of Technical and Pharmaceutical Schools.

By WILLIAM CALDWELL, M.A., Sc.D. With an Introduction by C. S. GIBSON, O.B.E., M.A., M.Sc. 436 pp. 8vo. 10s. 6d. (1924)

Bloxam's Chemistry—Inorganic and Organic, with Experiments.

By ARTHUR G. BLOXAM, F.I.C., Consulting Chemist and Chartered Patent Agent, and S. JUDD LEWIS, D.Sc., F.I.C., Consulting and Analytical Chemist. Eleventh Edition. 310 Illustrations. 842 pp. Royal 8vo. 36s. (1923)

Quantitative Organic Microanalysis.

By F. PREGL, D.Sc., Ph.D. Second Edition. Translated from third German Edition by E. FYLEMAN, B.Sc., Ph.D. 51 Illustrations. 252 pp. 15s. (1930)

Introduction to Chemical Analysis.

By HUGH C. H. CANDY, B.A., B.Sc. 126 pp. Crown 8vo. 3s. 6d. (1905)

The Fundamental Processes of Dye Chemistry.

By Dr. H. E. FIERZ-DAVID, Professor of Chemistry, Federal Technical High School, Zurich. Translated by F. A. MASON, M.A., Ph.D., Research Chemist, British Dyestuffs Corporation. 45 Illustrations, including 19 Plates. 254 pp. 8vo. 21s. (1921)

Organic Medicaments and their Preparation.

By Professor E. FOURNEAU. Translated by W. A. SILVESTER, M.Sc. With an Introduction by Professor G. BARGER, F.R.S. 22 Illustrations. 272 pp. 8vo. 15s. (1925)

A Systematic Handbook of Volumetric Analysis.

By FRANCIS SUTTON, F.I.C., F.C.S. Eleventh Edition, revised by W. LINCOLNE SUTTON, F.I.C., and A. E. JOHNSON, B.Sc., F.I.C. 120 Illustrations. 640 pp. 8vo. 35s. (1924)

Practical Physiological Chemistry.

By PHILIP B. HAWK, M.S., Ph.D., and OLAF BERGEIM, M.S., Ph.D. Tenth Edition. 288 Illustrations, 20 in colour. 948 pp. Royal 8vo. 32s. (1931)

A Manual for Masons, Bricklayers, Concrete Workers and Plasterers.

By J. A. VAN DER KLOES, Professor in the University at Delft. Revised and Adapted by ALFRED B. SEARLE. 81 Illustrations. 8s. 6d. (1914)

Chemistry of Carbon Compounds.

By HENRY WATTS, B.A., F.R.S. Second Edition. By Sir W. A. TILDEN. Crown 8vo. 10s. (1886)

Cocoa and Chocolate. Their Chemistry and Manufacture.

By R. WHYMPER. Second Edition. 16 Plates and 38 Text-figures. 584 pp. Royal 8vo. 42s. (1921)

J. & A. CHURCHILL LTD.

EXPLOSIVES

By ARTHUR MARSHALL, A.C.G.I., F.I.C., F.C.S., formerly Chemical Inspector, Indian Ordnance Department. Second Edition. With 157 Illustrations and Frontispiece to each Volume. 822 pp. Crown 4to. 63s. (1917)

Vol. I. **History and Manufacture.**
Vol. II. **Properties and Tests.**
Vol. III. **Supplementary and Revisionary Volume.** 14 Illustrations. 300 pp. Crown 4to. 42s. (1932)

By the same Author

A SHORT ACCOUNT OF EXPLOSIVES

29 Illustrations. 104 pp. Crown 4to. 7s. 6d. (1917)

and

A DICTIONARY OF EXPLOSIVES

174 pp. 8vo. 15s. (1920)

Chemical Combination among Metals.

By Dr. M. GIUA and Dr. C. GIUA-LOLLINI, Professor of General Chemistry in the Royal University of Sassari. Translated by G. W. ROBINSON, University College, Bangor. 207 Illustrations. 356 pp. 8vo. 21s. (1918)

The Plant Alkaloids.

By T. A. HENRY, D.Sc.Lond., Director, Wellcome Chemical Research Laboratories. Second Edition. 464 pp. 8 plates. 8vo. 28s. (1924)

The Analyst's Laboratory Companion. A Collection of Tables and Data for Chemists and Students, together with numerous examples of Chemical Calculations and concise Descriptions of several Analytical Processes.

By ALFRED E. JOHNSON, B.Sc.Lond., F.I.C., Assoc.R.C.Sc.I. Fifth Edition. 186 pp. Crown 8vo. 10s. 6d. (1920)

Introduction to Qualitative Chemical Analysis.

By C. REMIGIUS FRESENIUS. Seventeenth Edition. By Th. W. FRESENIUS. Translated by C. AINSWORTH MITCHELL, D.Sc., M.A., F.I.C. 57 Illustrations. 974 pp. 8vo. 36s. (1921)

Quantitative.

By C. REMIGIUS FRESENIUS. Seventh Edition. Vol. I. Translated by ARTHUR VACHER. 106 Engravings. 524 pp. 8vo. 18s. (1876)

Vol. II. Translated by CHARLES E. GROVES, F.R.S. 143 Engravings. 712 pp. 8vo. 24s. (1900)

Modern Methods of Cocoa and Chocolate Manufacture.

By H. W. BYWATERS, D.Sc., Ph.D., F.I.C., Director, Slade and Bullock (1929) Ltd., Dewsbury. 108 Illustrations. Royal 8vo. 326 pp. 21s. (1930)

Gas Works Laboratory Handbook.

By W. I. INESON, Chief Chemist, Bradford Corporation Gas Dept. 55 Illustrations. 184 pp. 8vo. 9s. 6d. (1926)

A Junior Inorganic Chemistry.

By R. H. SPEAR, B.A., Senior Chemistry Master, Swansea Grammar School. Second Edition. 97 Illustrations. 400 pp. Crown 8vo. 6s. 6d. (1927)

Also, separately,

Part I. **Up to Atomic Theory.**

46 Illustrations. 154 pp. Crown 8vo. 3s. 6d. (1920)

RECENT ADVANCES IN ATOMIC PHYSICS

By GAETANO CASTELFRANCHI, Professor in the High School for Engineers in Milan. Approved Translation by W. S. STILES, Ph.D., Scientific Assistant, National Physical Laboratory, Teddington, and J. W. T. WALSH, M.A., D.Sc., Principal Assistant, National Physical Laboratory, Teddington.

Vol. I. **Atoms, Molecules and Electrons.** 111 Illustrations, 384 pp. 8vo. 15s. (1932)

Vol. II. **The Quantum Theory.** 79 Illustrations. 422 pp. 8vo. 15s. (1932)

RECENT ADVANCES IN PHYSICS (NON-ATOMIC)

By F. H. NEWMAN, D.Sc., A.R.C.S., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter. 51 Illustrations. 388 pp. 8vo. 15s. (1932)

RECENT ADVANCES IN PHYSICAL CHEMISTRY

By S. GLASSTONE, D.Sc., Ph.D.Lond., F.I.C., Lecturer in Physical Chemistry, University of Sheffield. Second Edition. 33 Illustrations. 506 pp. 8vo. 15s. (1933

ELEMENTARY PHYSICS

For Medical, First Year University Science Students and General Use in Schools. By G. STEAD, M.A., F.Inst.P., Reader in Physics, University of London. Fourth Edition. 294 Illustrations. 470 pp. 8vo. 10s. 6d. (1933)

A Handbook of Physics and Chemistry.

By H. E. CORBIN, B.Sc.Lond., M.R.C.S., L.R.C.P., D.P.H., and A. M. STEWART, M.A., B.S.Lond. Fifth Edition. 200 Illustrations. 504 pp. Crown 8vo. 12s. 6d. (1920)

Physics for Students of Science and Engineering.

By A. WILMER DUFF, D.Sc., Professor of Physics, Polytechnic Institute, Worcester, Mass. Seventh Edition. 630 Figures. 698 pp. 8vo. 18s. (1932)

A Treatise on Physics.

By ANDREW GRAY, LL.D., F.R.S.

Vol. I. **Dynamics and Properties of Matter.** 350 Illustrations. 712 pp. 8vo. 18s. (1901)

The Physics of X-ray Therapy.

By W. V. MAYNEORD, M.Sc., Physicist to the Radio-Therapeutic Department of the Cancer Hospital, London. 106 Illustrations. 185 pp. 8vo. 10s. 6d. (1929)

Molecular Physics and the Electrical Theory of Matter.

By J. A. CROWTHER, Sc.D., F.Inst.P., Professor of Physics, University College, Reading. Fourth Edition. 34 Illustrations. 212 pp. Crown 8vo. 7s. 6d. (1927)

By the same Author

The Principles of Radiography.

55 Illustrations. 146 pp. 8vo. 7s. 6d. (1922)

RECENT ADVANCES IN CYTOLOGY

By C. D. DARLINGTON, D.Sc., Ph.D., Cytologist, John Innes Horticultural Institution. Foreword by J. B. S. HALDANE, M.A., F.R.S. 8 Plates, 109 Text-figures and 66 Tables. 578 pp. 8vo. 18s. (1932)

RECENT ADVANCES IN PLANT GENETICS

By F. W. SANSOME, Ph.D., F.L.S., F.R.S.E., and J. PHILP, B.Sc., F.L.S., Research Workers, the John Innes Horticultural Institution, Merton. With a Foreword by Sir DANIEL HALL, K.C.B., LL.D., D.Sc., F.R.S. 424 pp. 8vo. 55 Illustrations. 15s. (1932)

RECENT ADVANCES IN AGRICULTURAL PLANT BREEDING

By H. HUNTER, Hon. M.A.(Cantab.), D.Sc.(Leeds), Plant Breeding Institute, School of Agriculture, Cambridge, and H. MARTIN LEAKE, M.A., Sc.D.(Cantab.), Formerly Director of Agriculture, United Provinces, India. With a Foreword by SIR ROWLAND H. BIFFEN, M.A., F.R.S. With 16 Plates. 372 pp. 8vo. 15s. (1933)

RECENT ADVANCES IN BOTANY

By E. C. BARTON-WRIGHT, M.Sc.(Lond.), F.R.S.E., Chief Assistant at the Scottish Society for Research, in Plant Breeding, Corstorphine.

60 Illustrations. 396 pp. 8vo. 12s. 6d. (1932)

By the same Author

RECENT ADVANCES IN PLANT PHYSIOLOGY

Second Edition. 54 Illustrations. 352 pp. 8vo. 12s. 6d. (1933)

A Text-book of Botany.

For Medical, Pharmaceutical and other Students.

By JAMES SMALL, D.Sc., Ph.C., F.L.S., F.R.S.(Edin.), Professor of Botany, Queen's University, Belfast. Third Edition. Over 1,350 Illustrations. 728 pp. 8vo. 21s. (1933)

By the same Author

Practical Botany.

For Medical, Pharmaceutical and other Students.

35 Illustrations. 328 pp. 8vo. 10s. 6d. (1931)

and

Pocket Lens Plant Lore, Month by Month.

Over 700 Original Drawings. 232 pp. Crown 8vo. 5s. (1931)

A Text-book of Mycology and Plant Pathology.

By J. W. HARSHBERGER, Ph.D. 271 Illustrations. 794 pp. 8vo. 24s. (1918)

Plant Anatomy and Handbook of Micro-Technic.

By WILLIAM CHASE STEVENS, 4th Edition. 155 Engravings. 400 pp. 8vo. 21s. (1924)

The Story of Plant Life in the British Isles.

By A. R. HORWOOD. 3 Vols. Illustrated. Crown 8vo. 6s. 6d. each. (1914), (1915)

An Introduction to Vegetable Physiology.

By J. REYNOLDS GREEN, Sc.D., F.R.S. Third Edition. 182 Illustrations. 492 pp. 8vo. 12s. 6d. (1911)

RECENT ADVANCES IN THE STUDY OF PLANT VIRUSES

By KENNETH M. SMITH, D.Sc.(Manch.), Ph.D.(Cantab.), Potato Virus Research Station, School of Agriculture, Cambridge. 1 Coloured Plate and 67 Text-figures. 436 pp. 8vo. 15s. (1933)

THE SCIENCE AND PRACTICE OF PHARMACY

By R. R. BENNETT, B.Sc., F.I.C., and T. T. COCKING, F.I.C.

Vol. I. **Pharmaceutical Operations and the Manufacture of Pharmacopœial Substances.** 166 Illustrations. 394 pp. Royal 8vo. 18s. (1933)

Vol. II. **The Physical and Chemical Examination of Pharmacopœial Substances.** 72 Illustrations. 348 pp. Royal 8vo. 18s. (1933)

RECENT ADVANCES IN MATERIA MEDICA

Being a description of the methods of preparing and testing Sera and Vaccines, Hormones and Vitamins, with an account of their Properties and Medicinal Uses.

By J. H. BURN, M.A., M.D.(Cantab.), Dean of the College of the Pharmaceutical Society of Great Britain. 25 Illustrations. 234 pp. 8vo. 12s. 6d. (1932)

RECENT ADVANCES IN CHEMOTHERAPY

By G. M. FINDLAY, O.B.E., D.Sc., M.D., Wellcome Bureau of Scientific Research, London. 4 Plates and 11 Text-figures. 532 pp. 8vo. 15s. (1930)

By E. W. LUCAS, C.B.E., F.I.C., F.C.S., Late Examiner to the Pharmaceutical Society, and H. B. STEVENS, O.B.E., F.I.C., F.C.S., Late Lecturer on Pharmacy, South Western Polytechnic Institute.

THE BOOK OF PRESCRIPTIONS

With Notes on the Pharmacology and Therapeutics of the more important Drugs and an Index of Diseases and Remedies.

Eleventh Edition. 392 pp. F'cap. 8vo. 10s. 6d. (1926)

THE BOOK OF RECEIPTS

Containing a Veterinary Materia Medica, comprising also a Pharmaceutical Formulary, a Photographic Formulary, etc.

Twelfth Edition. 480 pp. Crown 8vo. 10s. 6d. (1924)

PRACTICAL PHARMACY

Third Edition. With 224 Illustrations. 432 pp. Royal 8vo. 27s. (1921)

THE BOOK OF PHARMACOPŒIAS AND UNOFFICIAL FORMULARIES

Containing the Formulas of the British, United States, French, German and Italian Pharmacopœias, together with Formulas from Unofficial Sources, comprising about 5,000 Formulas.

532 pp. Crown 8vo. 7s. 6d. (1915)

PRINCIPLES OF PHARMACY

By HENRY B. MACKIE, B.Pharm., Ph.C., Member of Board of Examiners for England and Wales of the Pharmaceutical Society; Head of the Pharmacy Department, Brighton Technical College. 67 Illustrations. 296 pp. 8vo. 10s. 6d. (1932)

A TEXT-BOOK OF PHARMACOGNOSY

Being an Account of the more important Crude Drugs of Vegetable and Animal Origin. Designed for Students of Pharmacy and of Medicine.

By HENRY G. GREENISH, D. ès Sc., F.I.C., F.L.S., Late Professor of Pharmaceutics to the Pharmaceutical Society of Great Britain, and Director of the Pharmacy Research Laboratory. Sixth Edition. 297 Illustrations. 578 pp. Roy. 8vo. 25s. (1933)

FIRST LINES IN DISPENSING

By H. B. STEVENS, O.B.E., F.I.C., F.C.S., and C. E. L. LUCAS, A.I.C., F.C.S. Third Edition. 95 Illustrations. 198 pp. 8vo. 7s. 6d. (1930)

The Cyclopædia of Practical Receipts, and Collateral Information in the Arts, Manufactures, Professions, and Trades, including Medicine, Pharmacy, Hygiene, and Domestic Economy.

By ARNOLD J. COOLEY. Seventh Edition. By WILLIAM NORTH, M.A., F.C.S. 371 Engravings. 2 Vols. 1,827 pp. 8vo. £2 10s. (1892)

The Pharmaceutical Formulary.

By HENRY BEASLEY. Twelfth Edition. Edited by J. OLDHAM BRAITHWAITE. 470 pp. 18 mo. 6s. 6d. (1899)

An Anatomical Atlas of Vegetable Powders.

By Professor H. G. GREENISH and EUGÈNE COLLIN. 138 Illustrations. 288 pp. 4to. 12s. 6d. (1904)

Practical Pharmacognosy.

By T. E. WALLIS, B.Sc., F.I.C., Ph.C., Reader in Pharmacognosy, University of London. Foreword by Professor H. G. GREENISH, D.ès Sc., F.I.C., F.C.S. Second Edition. 105 Illustrations. 208 pp. 8vo. 12s. 6d. (1931)

Volumetric Analysis for Pharmaceutical Students.

By C. H. HAMPSHIRE, M.B., B.S., B.Sc.Lond., F.I.C. Ph.C. Fifth Edition. 204 pp. Crown 8vo. 8s. 6d. (1933)

ADULTERATION AND ANALYSIS OF FOODS AND DRUGS

Birmingham Methods and Analyses of Samples. Review of British Prosecutions during Half a Century.

By J. F. LIVERSEEGE, F.I.C., Ph.C., Formerly Public Analyst to the City of Birmingham. Foreword by The Rt. Hon. NEVILLE CHAMBERLAIN, M.P., Formerly Minister of Health. 616 pp. Roy. 8vo. 36s. (1932)

Synopsis of Hygiene.

By W. WILSON JAMESON, M.D., F.R.C.P., D.P.H., of the Middle Temple, Barrister-at-Law, Professor of Public Health, London University, and G. S. PARKINSON, *D.S.O.*, M.R.C.S., L.R.C.P., D.P.H., Lt.-Col. R.A.M.C. (Ret.), Assistant Director of Public Health Division London School of Hygiene and Tropical Medicine. Fourth Edition. 17 Illustrations. 620 pp. 8vo. 21s. (1934)

The Principles of Preventive Medicine.

By R. TANNER HEWLETT, M.D., F.R.C.P., D.P.H., and A. T. NANKIVELL, M.D., D.P.H. 12 Charts and 5 Diagrams. 544 pp. 8vo. 18s. (1921)

Preservatives in Food, and Food Examination.

By J. C. THRESH, M.D., and A. E. PORTER, M.D. 8 Plates. 499 pp. Royal 8vo. 16s. (1906)

The Health of the Industrial Worker.

By E. L. COLLIS, B.Ch., M.D., and M. GREENWOOD, F.R.C.P., F.R.S. Introduction by Sir GEORGE NEWMAN, K.C.B., D.C.L., M.D. 38 Illustrations. 464 pp. Royal 8vo. 30s. (1921)

Malay Poisons and Charm Cures.

By JOHN D. GIMLETTE, M.R.C.S., L.R.C.P. Third Edition. 3 Illustrations. 316 pp. 8vo. 10s. 6d. (1929)

Sanitation in War.

By Lt.-Col. P. S. LELEAN, C.B., C.M.G., F.R.C.S., D.P.H., R.A.M.C. Third Edition. 68 Illustrations. 376 pp. F'cap 8vo. 7s. 6d. (1919)

Elementary Hygiene for Nurses.

By H. C. R. DARLING, M.D., F.R.C.S., Surgeon, Coast Hospital, Sydney. Fifth Edition. 58 Illustrations. 326 pp. 8vo. 5s. (1932)

Recent Advances in Preventive Medicine.

By J. F. C. HASLAM, *M.C.*, M.D., M.R.C.P.(Edin.), D.P.H., formerly Government M.O.H., British Guiana. 30 Illustrations. 325 pp. 8vo. 12s. 6d. (1930)

Beverages and their Adulteration.

Origin, Composition, Manufacture, Natural, Artificial, Fermented, Distilled, Alkaloidal and Fruit Juices.

By HARVEY W. WILEY, M.D., Ph.D. 42 Illustrations. 438 pp. 8vo. 21s. (1919)

PUBLIC HEALTH PRACTICE IN THE TROPICS

By J. BALFOUR KIRK, M.B., D.P.H., D.T.M. & H., Director, Medical and Health Department, Mauritius. 80 Illustrations. 510 pp. Demy 8vo. 15s. (1930)

J. & A. CHURCHILL LTD.

RECENT ADVANCES IN MICROSCOPY

(Biological Applications)

Edited by A. PINEY, M.D., M.R.C.P.

Sections: **The Medical Sciences,** by Dr. A. PINEY; **Microscopy of the Living Eye,** by BASIL GRAVES, *M.C.*, M.R.C.S., D.O.M.S.(Eng.); **Zoology,** by E. W. MacBRIDE, LL.D., D.Sc., F.R.S., and H. R. HEWER, A.R.C.S., D.I.C., M.Sc.; **Botany,** by E. C. BARTON-WRIGHT, M.Sc.
3 Illustrations. 270 pp. 8vo. 12s. 6d. (1931)

ELEMENTARY HISTOLOGICAL TECHNIQUE FOR ANIMAL AND PLANT TISSUES

By J. T. HOLDER, F.R.M.S. 23 Illustrations. 112 pp. 8vo. 7s. 6d.

BOLLES LEE'S MICROTOMIST'S VADE-MECUM

A handbook of the Methods of Microscopic Anatomy.

Edited by J. BRONTË GATENBY, D.Sc.(Lond.), F.R.M.S., and E. V. OWDRY, M.A., Ph.D. Ninth Edition. 720 pp. 8vo. 30s. (1928)

RECENT ADVANCES IN TOWN PLANNING

By THOMAS ADAMS, F.S.I., F.I.L.A., Past President, Town Planning Institute; Member of the Board of Governors, American City Planning Institute, In collaboration with F. LONGSTRETH THOMPSON, B.Sc., .P.T.P.I., F.S.I., E. MAXWELL FRY, B.Arch., A.R.I.B.A., and JAMES V. R. ADAMS, A.M.T.P.I. 2 Coloured Maps and 87 Illustrations. 416 pp. Crown 4to. 25s. (1932)

RECENT ADVANCES IN ENTOMOLOGY

By A. D. IMMS, M.A., D.Sc., F.R.S., Reader in Entomology, University Cambridge. 84 Illustrations. 382 pp. 8vo. 12s. 6d. (1930)

THE NEMATODE PARASITES OF VERTEBRATES

By WARRINGTON YORKE, M.D., F.R.S., and P. A. MAPLESTONE, I.B., D.S.O. Foreword by C. W. STILES, Professor of Zoology, United States Public Health Service. 307 Illustrations. 548 pp. Royal 8vo. 6s. (1926)

TEXT-BOOK OF MEAT HYGIENE

With Special Consideration of Ante-mortem and Post-mortem Inspection of Food-producing Animals.

By RICHARD EDELMANN, Ph.D., Professor at the Royal Veterinary High School, Dresden. Authorised Translation by J. R. MOHLER, A.M., .M.D., and A. EICHHORN, D.V.S. Sixth Edition. 5 Coloured Plates and 62 Illustrations. 480 pp. 8vo. 28s. (1934)

THE COMPARATIVE ANATOMY OF THE DOMESTICATED ANIMALS

By A. CHAUVEAU, M.D., LL.D., and S. ARLOING. Translated and Edited by GEORGE FLEMING. Second Edition. 585 Engravings. 1,084 pp. 8vo. 35s. (1891)

ADAMS, T. 15
Allen, A. H. 2
Appleyard, F. N. 3
Arloing, S. 15
Arnall, F. 3
Arup, P. S. 4, 12
Autenreith, W. 4

BARNETT, E. de B. 4
Barton-Wright, E. 9, 15
Beale, J. F. 12
Beasley, H. 11
Bennett, R. R. 10
Bergeim, O. 6, 13
Bloxam, A. G. 6
Bloxam, C. L. 6
Bolton, E. R. 3
Braithwaite, J. O. 11
Burn, J. 10
Burns, D. 13
Bywaters, H. W. 7

CALDWELL, W. 6
Cameron, A. T. 13
Candy, H. 6
Carpenter, J. A. 4
Castelfranchi, G. 8
Chauveau, A. 15
Clayton, W. 2, 5
Clowes, F. 3
Cocking, T. T. 10
Coleman, J. B. 3
Collin, E. 11
Collis, E. L. 14
Cooley, A. 11
Corbin, H. E. 8
Cowdry, E. V. 15
Cox, H. E. 3
Crookes, Sir W. 4
Crowther, J. A. 5, 8

DARLING, H. C. R. 14
Darlington, C. D. 9
Dexter, J. 3
Dible, J. H. 12
Dreaper, W. P. 5
Duff, A. W. 8

EDELMANN, R. 15
Eichhorn, A. 15

FIERZ-DAVID, H. E. 6
Findlay, G. M. 10
Fleming, G. 15
Fourneau, E. 6
Fowweather, F. S. 12
Fresenius, R. 7
Fyleman, E. 5, 6

GATENBY, J. B. 15
Gibbs, W. E. 5
Gilmour, C. R. 13
Giltner, W. 12
Gimlette, J. D. 14
Giua, M. 7
Glasstone, S. 8
Graves, B. 15
Gray, A. 8
Green, J. R. 9
Greenish, H. G. 11
Greenwood, M. 14
Groves, C. E. 7

HACKH, I. 2
Hampshire, C. H. 11
Harrison, G. A. 12
Harshberger, J. W. 9
Haslam, J. F. C. 14
Hatschek, E. 5
Hawk, P. B. 6, 13
Henry, T. A. 7
Hewer, H. R. 15
Hewlett, R. T. 12, 14
Hodges, F. W. 3
Hodgkinson, W. R. 4
Holder, J. T. 15
Hood, G. F. 4
Horwood, A. R. 9
Hunter, H. 9

IMMS, A. D. 15
Ineson, W. I. 7

JAMESON, W. W. 14
Jensen, H. R. 2
Jobling, E. 5
Johnson, A. E. 6, 7
Johnston, J. H. 12

KIRK, J. B. 14
Kloes, J. A. van der 6

LATHROP, E. C. 2
Leake, H. M. 9
Lee, A. B. 15
Lelean, P. S. 14
Lewis, S. Judd 6
Liverseege, J. F. 14
Lloyd, D. J. 3
Lucas, C. E. L. 11
Lucas, E. W. 10
Lyons, C. G. 3

MACBRIDE, E. W. 15
Macfadyen, A. 13
Mackie, H. B. 11
Maplestone, P. A. 15
Marshall, A. 7
Marshall, C. E. 12
Mason, F. A. 6
Maxted, E. B. 5
Mayneord, W. V. 8
McIntosh, J. 12
Mitchell, C. A. 2, 5, 6, 7
Mohler, J. R.
Molinari, E.

NANKIVELL, A. T.
Newman, F. H.
Nierenstein, M.
North, W.

ORLA-JENSEN

PARKINSON, G. S.
Parry, E. J.
Pauli, W.
Philp, J.
Piney, A.
Pope, T. H.
Porter, A. E.
Pregl, F.
Pryde, J.

ROBINSON, G. W.
Robson, J. M.

SADTLER, S. S.
Sansome, F. W.
Searle, A. B.
Silvester, W. A.
Simpson, R. H.
Small, J.
Smith, K. M.
Spear, R. H.
Stead, G.
Stevens, H. B. 10,
Stevens, W. C.
Stewart, A. M.
Stiles, W. S.
Stockdale, D.
Suckling, E.
Sutton, F.
Sutton, W. L.
Svedberg, T.

THORNE, P. C. L.
Thresh, J. C. 12,
Tilden, Sir A. W.
Tognoli, E.

VACHER, A.
Valentin, W. G.
Villavecchia, V.

WAESER, B.
Wagner, R.
Wallis, T. E.
Walsh, J. W. T.
Warren, W. H.
Watts, H.
Whitby, L. E. H. 1
White, F. D. 1
Whymper, R.
Wiley, H. W. 1
Williams, H. E.

YORKE, Warrington 1